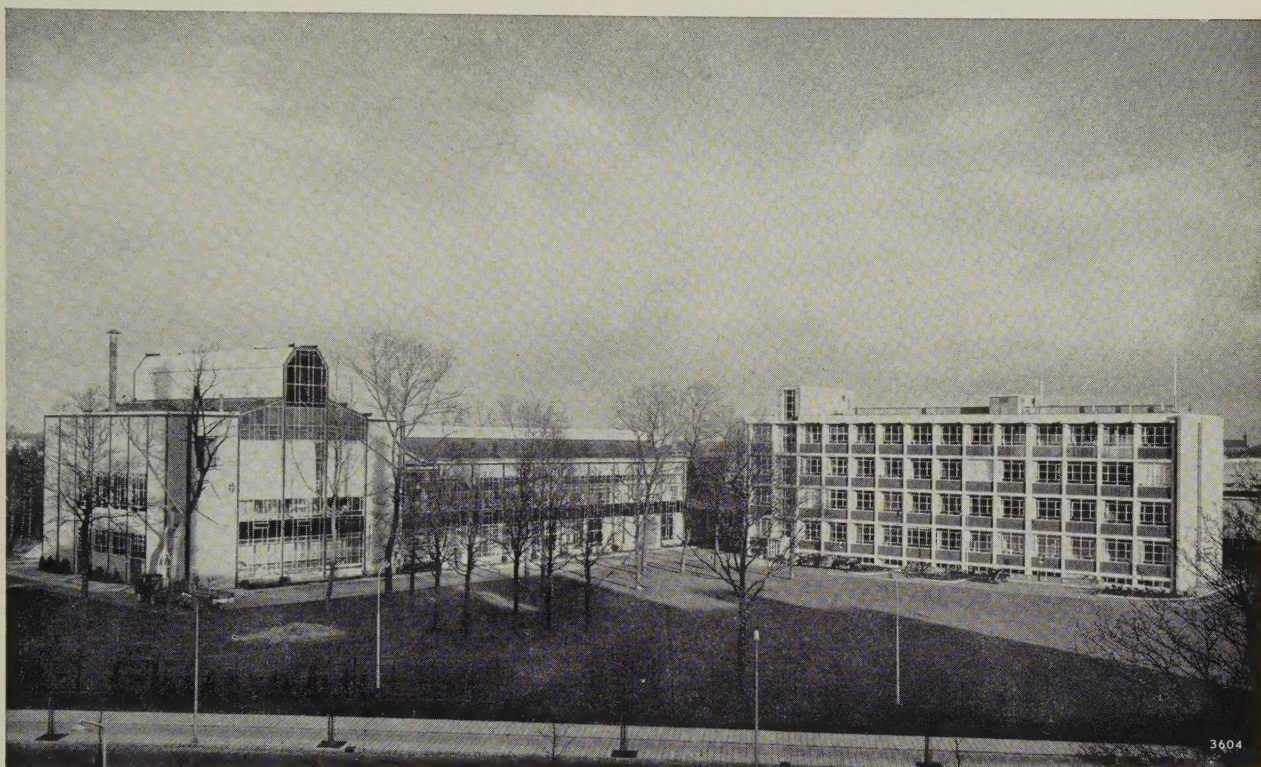


Philips Technical Review

DEALING WITH TECHNICAL PROBLEMS
RELATING TO THE PRODUCTS, PROCESSES AND INVESTIGATIONS OF
THE PHILIPS INDUSTRIES



This issue of our journal is entirely devoted to the material "glass" — one of the most important of the materials used in the manufacture of Philips products. Glass, in multifarious kinds and shapes, has here traditionally served the purpose of "vacuum-packaging material". The preparation and processing of glass — the modern melting furnaces with their ancillary equipment, and bulb-blowing machines, remarkable examples of mechanization — will be discussed in this issue along with the still continuously evolving theoretical views concerning the structure of glass, including such surprising ideas as the invert glasses and the "amorphous substance with lattice imperfections". A short, concluding article deals with glass-metal seals and with manufacturer-user relations in this connection.

This series of articles is prefaced by a concise historical survey of the uses which mankind has made of glass in the last 7000 years. We believe that articles of this kind are useful, not only to the historian but also to the engineer and to the man of science, helping them to see their own work and the work of others in a broader perspective. The survey presented here was written at our request by Professor Forbes of the University of Amsterdam, a distinguished authority on the history of technology.

To lend relief to the idea underlying this survey — the evolution from empiricism to science — our title photograph shows the Glass Development Centre, Eindhoven, opened in 1957, where glass research and the development of new manufacturing methods for the Philips glass factories are largely concentrated.

GLASS THROUGHOUT THE AGES

by R. J. FORBES *).

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Glass at the dawn of history

From the many modern types of glass and their applications, numerous threads run back through the course of history to a single point, the invention of glass-blowing in the first century before the Christian era. Only from that time onwards can glass rightfully be regarded as an independent material of common utility. Nevertheless, glass processed by a variety of more primitive methods had already

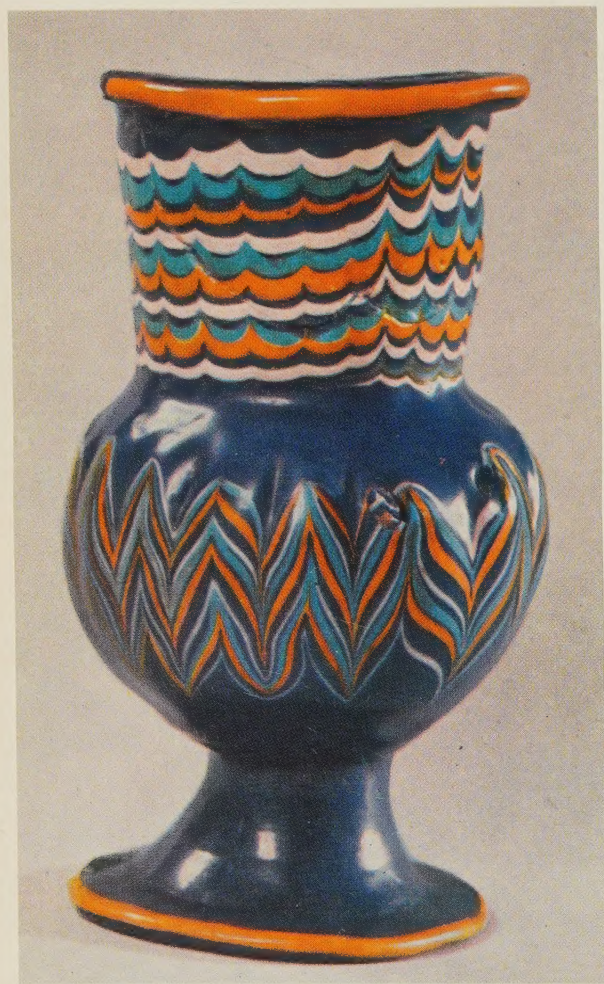


Fig. 1. Egyptian unguent jar from the eighteenth dynasty (c. 1500-1350 B.C., probably made by modelling a softened layer of glass in a mould. Reproduced actual size. (Courtesy of Rijksmuseum van Oudheden, Leyden.)

been in use from the most ancient times, principally for decorative purposes.

It is certain that glazed pottery was being made in the Near East as early as 5000 B.C. The glaze applied to the pottery was prepared by the fusion of silica (quartz) sand, shell lime or magnesian limestone and "alkali". The alkali used in Egypt was usually the natural soda extracted from the oases of the Western Desert; in Phoenicia and Mesopotamia it was soda ash gained from seaweed and alkaline plants. In this way even prehistoric man applied glassy coatings to brightly coloured semiprecious stones and pebbles. Variegated colouring was obtained by the addition of small quantities of copper, iron and other minerals.

Round about 1500 B.C. more and more small objects made entirely of glass began to appear in Egypt and Mesopotamia. They were made by four techniques ¹⁾.

- 1) Beads or small pieces of glass were cast in moulds, and used for jewellery, mosaics or cloisonné work. Beads of this kind were exported throughout prehistoric Europe, and their shape and style now often enable the archeologist to date his finds. The technique of making these beads and imitation stones went from Mesopotamia to China, where they remained in vogue for centuries; long after, in the 18th century A.D., the technique was still used in China for making ornamental figures and small perfume flasks, which were exported to Europe.
- 2) A layer of hot, softened glass was pressed into shape in a mould. This technique was related to the ancient method of making faience earthenware by modelling a siliceous powder mixed with milk of lime (the heating in that case, however, being applied after the shaping). A spectacular example is the famous blue-glass neck-support found in 1922 in Tutenkhamon's tomb (14th century B.C.). In the residence of this pharaoh at El Amarna the remains of a complete glass workshop have been excavated. An Egyptian moulded vial of the period made in this way is shown in *fig. 1*.

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¹⁾ R. J. Forbes, *Studies in ancient technology*, Vol. V, E. J. Brill, Leyden 1957.

3) Quite large arbitrarily shaped and sometimes coloured lumps of glass were cast (e.g. in clay crucibles) and then cut in the manner of rock crystal to form amulets or ornaments. Examples of this technique are known only from Mesopotamia, the oldest being a small vase inscribed with the name of King Sargon II (700 B.C.), shown in *fig. 2*.

4) Rods of softened glass were modelled around a core of sand and then reheated to fuse them together, after which the sand was removed. Sometimes disks were cut from the still warm, coloured glass rods and arranged around a core; they were then fired together to form a vase or bowl ("millefiori" technique, see *fig. 3*). The vials, unguent jars and perfume flasks made by this process were very popular with the ancient Greeks and Romans, and the history of the millefiori technique is closely bound up with that of the cosmetics industry.

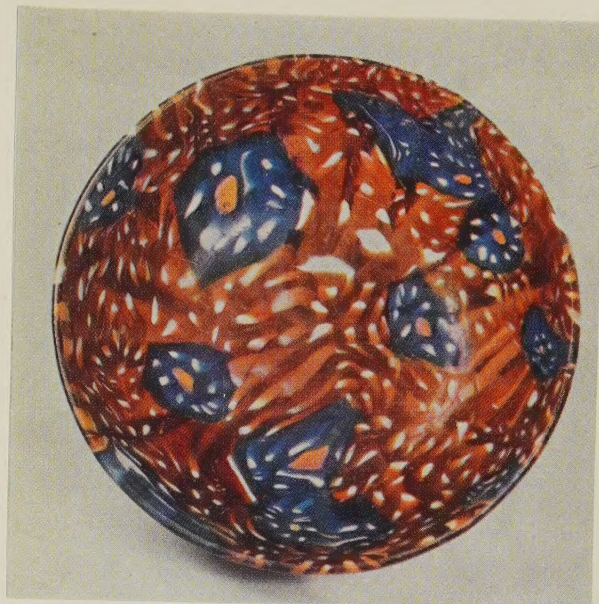


Fig. 3. Millefiori bowl from the first century A.D.; diameter 5.7". Found at Nijmegen. (Courtesy of Rijksmuseum van Oudheden, Leyden.)

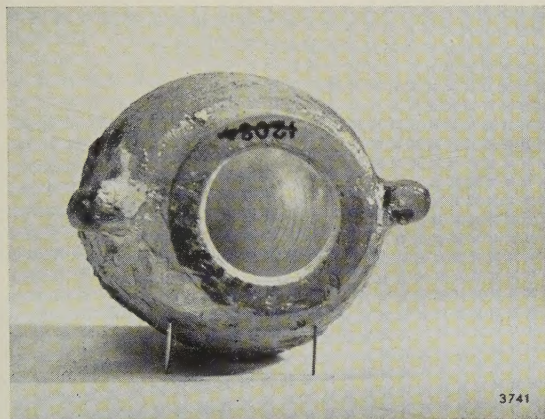


Fig. 2. Glass vase (height about 6") bearing in cuneiform script the name of King Sargon II of Assyria (700 B.C.); found at Nimrud. The interior grooves demonstrate that the vase was ground from a solid block of glass. (Courtesy of British Museum, London.)

Early texts on glass-making, dating back to 1700-700 B.C. (*fig. 4*) and originating not from Egypt but from Assyria, give detailed information on furnaces and smelting procedures, with recipes for a crude glass which was fused with colouring minerals to produce glazes or coloured glass. The basis is still sand-soda-lime glass, which was being made in Phoenicia at least six centuries before Christ. And it was there, in about 50 B.C., that the decisive discovery was made — the blowing of glass.

From ornament to utility material

The invention of glass-blowing, which was probably first done in a mould but was very soon followed by free or "off-hand" blowing, revealed new potentialities and properties of glass as a material. This led to a much greater diversity of shapes and designs (*fig. 5*) and also to the use of glass in homes and workshops, together with or instead of metal and earthenware. It was especially the possibility of making glass which was *transparent* and not merely translucent that opened up new prospects for science and daily life.

Whether the decisive factor was the ease of working and shaping the material, or its useful and decorative properties, is difficult to say; at all events the use of glass now widened rapidly.

Within a century of the invention of soda-lime glass-blowing, the art had spread via Persia to the Orient. In the West, Syrian, Jewish and Alexandrian glass-blowers were to be found in Rome and the districts south of the capital, in the valleys of the Rhône and the Saône, and in the Rhine province.

From there the art spread to Spain, to the border districts of the Low Countries and Gaul — where timber for the furnaces was plentiful — and to Britain. The primitive methods of pressing the glass in a mould or shaping it around a core still persisted, but off-hand blowing was the most important technique. Glass-cutting established itself as a separate

continued to flourish in ancient Alexandria, the centre of the cosmetics industry. A novel decorative technique was based directly on blowing: the *hot* lump of glass on the blowpipe was blown out into a mould, and after repeated immersion in various molten glasses and re-blowing, layered glass objects were produced. Ribs or grooves could be

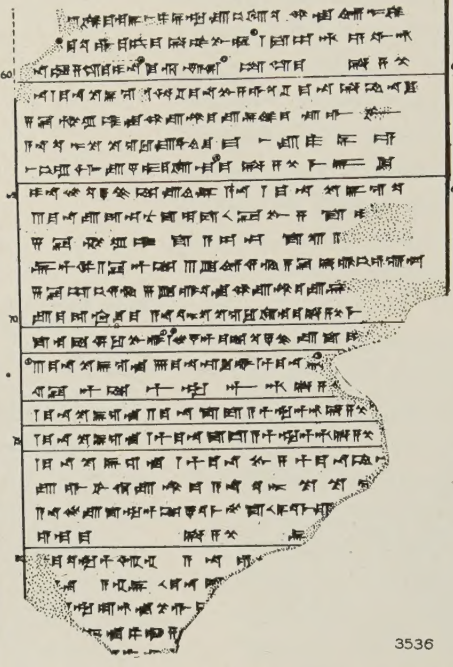
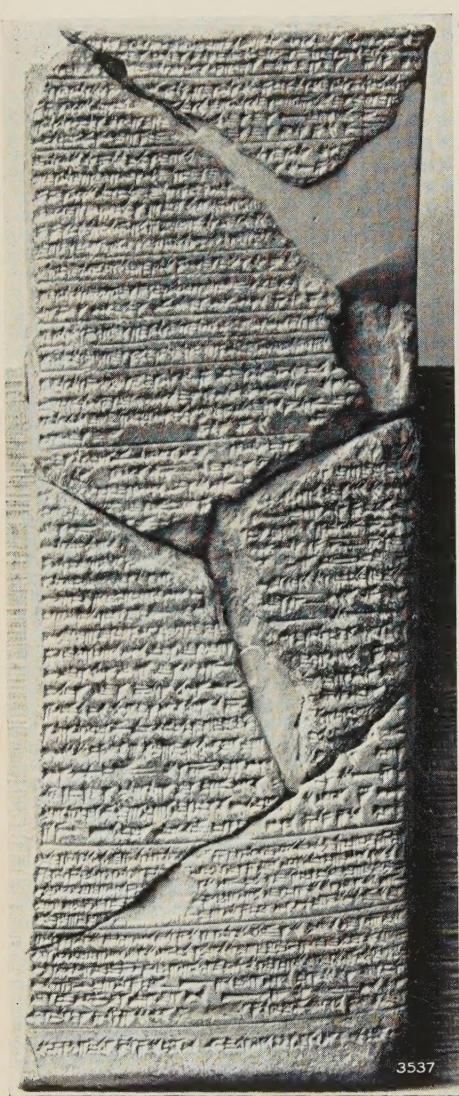


Fig. 4. The earliest document on glass-making: Mesopotamian cuneiform tablet from the seventeenth century B.C., giving recipes for making various kinds of glass and glazes. Left, photo with transcription beside it; right, translation of the first twenty lines. Investigators have followed the recipes and proved their validity (and the correctness of the translation); see p.131 et seq. of book cited in reference ¹). (Photograph by courtesy of British Museum, London.)

1. To a mina of zukû-glass (thou shalt add) 10 shekels of lead,*)
2. 15 shekels of copper, ½ a shekel of lime,
3. thou shalt put (it) down into the kiln (and) shalt take out santu (red) glass of lead.
4. To a mina of zukû-glass (thou shalt add) 1/6th (mina) of lead,
5. 14 shekels of copper, 2 shekels of lime, a shekel of saltpetre:
6. Thou shalt put (it) down into the kiln (and) shalt take out Accadian santu (red) glass.
7. (Thou shalt) green the clay and in vinegar and copper shalt thou keep it.
8. At the third (day) of thy keeping
9. it will deposit a bloom and thou shalt take (it) out.
10. Thou shalt continuously pour it off and it will dry and
11. thou shalt shape it. If it is (like) marble, be not troubled.
12. Accadian santu-glass and (that of) lead
13. thou shalt take in equal parts, and
14. triturate them together.
15. After thou hast melted them together,
16. into 1 mina of the melt a shekel and a half of zukû-glass,
17. 7½ grains of saltpetre, 7½ grains of copper, 7½ grains of lead
18. shalt thou triturate together and
19. thou shalt melt and keep it (so for) one (day?)
20. and shalt take it out and cool it

*) 1 mina (505 grammes) = 60 shekels = 10800 grains (of barley). The Assyrian scales were certainly correct to within 5 milligrammes!

art, practised not by the “vitrearii” (glass-blowers) but by the “diatretarii” (glass-cutters), whose techniques sprang from the much older skills of working rock crystal and precious stones ²).

In the numerous objects that have come down to us from that period we see the application of a variety of decorative techniques. The old millefiori process

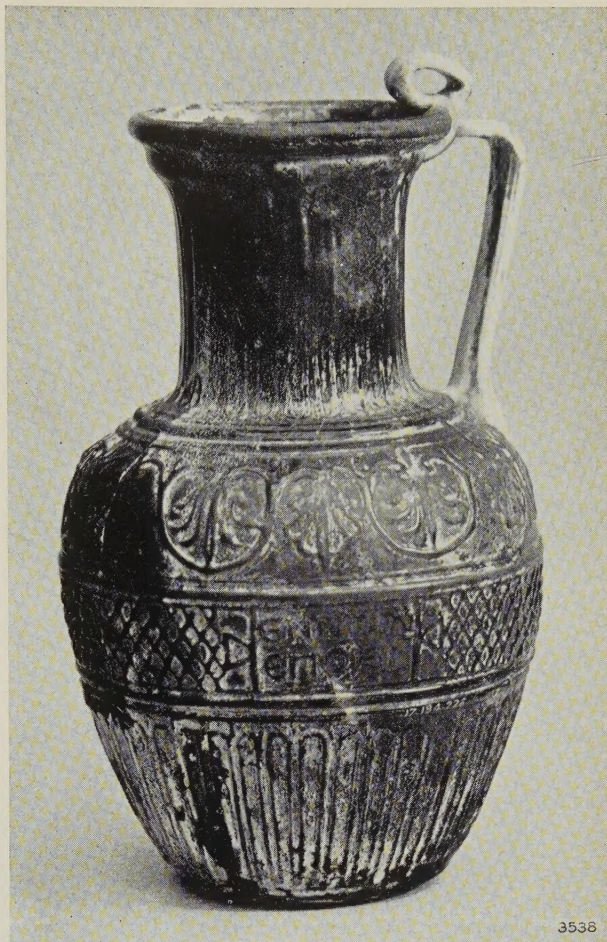
tooled into the shaped objects whilst still *warm*, or glass bosses or threads applied as decoration. The glass could also be *cold*-worked by polishing, painting or enamelling, and gold-leaf might be applied, often sandwiched between two glass layers. Finally, cold glass could be hollow-ground by the glass-cutters and provided with facets with a rotary grindstone and emery; the surface could be given a relief finish or it could be engraved. The latter was done with obsidian or similar hard stone, diamond

²) Much of our knowledge of glass in those times comes from Pliny, particularly from the 26th book of his “Natural History”.

Fig. 5. Mould-blown yellow glass jug, dating from early in the first century A.D. Shortly before this time, off-hand (free) blowing must also have been invented. The jug bears the signature "Ennion", the name of a Syrian glass-blower whose products have been unearthed at numerous places in the Roman Empire of that time. (Courtesy of Metropolitan Museum of Art, New York.)

being unknown in Antiquity. An example of what these craftsmen could achieve with relatively simple means can be seen in *fig. 6*.

Decorated blown glassware first made its appearance in the homes of rich Romans as a rival to gold and silver ware. At the same time, millefiori flasks, bowls and trinkets were being imported into Rome from Alexandria. The earliest glassware was almost as dear as cut rock crystal, but round about 75 A.D. prices began to drop as a result of the quantity production of simple tableware in addition to fine glass. The glass workshops became so numerous that in Rome, from 200 A.D., the glass-blowers were concentrated in the suburbs of Mons Caelius because the smoke from their furnaces had become a nuisance. An organized trade even sprang up in broken glass, which thus found its way back to the glass works. Around this time glassware on a Roman table was in fact a sign of poverty! A similar trend took place in about 200 A.D. in the Near East, and finds in the excavations at Karanis (Fayum, Egypt)



bear witness to the versatility of Alexandrian glass-blowers, even in the production of simple glassware for daily use. During the persecution of the Christians under Diocletian (300 A.D.) the headman of an Egyptian village declared that his community was poor and could therefore only afford altar vessels of glass. In the West a similar situation arose much later: in about 850 A.D. Pope Leo V forbade the use of glassware for celebrating Mass since it had become too cheap and debased a material.

Fig. 6. Roman "cage cup" (height 7") found in 1950 in a stone sarcophagus at Niederemmel near Trier, probably made at the Cologne glassworks towards the end of the third or the beginning of the fourth century A.D. Cage cups, cut from a single, originally thick-walled, glass beaker, probably represent the pinnacle of the glass-cutters' art. The technique adopted is discussed in detail by F. Fremersdorf, *Schuhmacher-Festschrift*, Mainz 1930. (Courtesy of Rheinisches Landesmuseum, Trier.)

Europe discovers new kinds of glass

The glass industry which had grown up in Gaul and in the Rhineland flourished for several centuries. Thriving centres of production were established notably in Cologne and Trier (cf. fig. 6) which, in about 300 A.D., ranked third among the cities of the Roman Empire. It was here, probably from a Germanic word for amber (or generally for a transparent, lustrous substance) that the late-Latin term *glesum* originated, to which we owe our own word “glass”.

The barbarian invasions and the fall of the Roman Empire in the West temporarily put an end to the development of the glass industry in Central Europe. Glass-blowers were still to be found in the cities along the Rhine and the Rhône, but many of them retreated to the comparative safety of Italy, in particular to the Po valley and to l’Altare (near Genoa), from where they later spread out again all over Europe. The gradual revival of glass crafts-

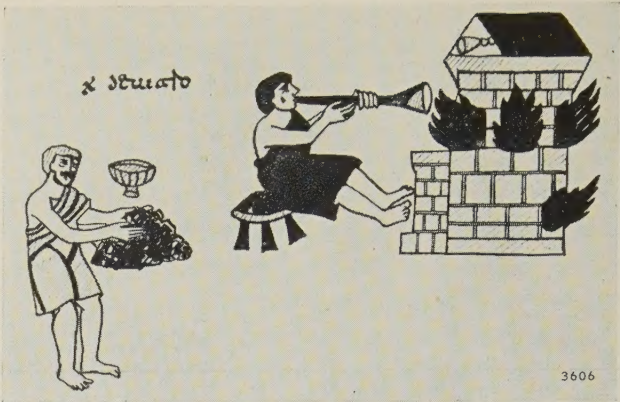


Fig. 7. Picture of a glass furnace, given by Hrabanus Maurus³⁾.

manship in the Frankish Empire was partly due to the churches and monasteries, which not only acted as the wardens of ancient knowledge but were also the patrons of new and extensive applications of glass, for example glass mosaics and stained-glass windows — though its use was not approved



Fig. 8. Painted mosque lamp from Damascus, 1350. (Courtesy of Corning Museum of Glass, Corning, N.Y.)

for altar vessels. To Hrabanus Maurus (died 856 A.D.), Bishop of Mainz and Councillor to Charlemagne, we owe the description of glass production in those times³⁾ and the oldest picture of a glass furnace (fig. 7). The Rhenish glass industry was hampered by the difficulty of importing soda from the South, and had to resort to plant ash, which contained potassium. Later too, after the tenth century, this potash glass remained characteristic of Central Europe when the glass-blower's art spread to Thuringia, Bohemia, Saxony and Silesia, whilst soda glass continued to be made in the coastal districts. Techniques, however, underwent very little change, partly owing to the lack of knowledge of glass chemistry. The most that can be said is that other forms appeared, such as the "tumbler" type of drinking glass. The earliest handbooks on glass making, by Heraclius and Theophilus from the ninth and tenth century⁴⁾, disclose an unbroken tradition going back over at least 1500 years.

In the East, too, the tradition remained unbroken, even after the emergence of Islam. The same decorative technique as used for rock crystal remained in vogue, and beautifully painted, gilded and enamelled Islamic glassware was produced (fig. 8), some of which found its way into the treasury repositories of mediaeval cathedrals. The arrival of the Mongols saw the application of Chinese decorative elements to this glassware, but at the same time it provoked the flight of many glass-blowers from Damascus and Aleppo to the West. Here, Venice had become an important glass centre since the commissioning of glass-blowers from Constantinople (about 1050) to make the mosaics for San Marco. In about 1200 they formed a powerful guild which, in 1291, settled on the island of Murano, with the idea that such isolation would better preserve their secrets. The secrets of their fabrication process were so jealously guarded that the emigration of guild members was forbidden on pain of death. On Murano the privileged glass-blowers made decorative tableware from soda glass, which had to compete with the products of gold and silver smiths; from 1500 they followed old Roman and Eastern styles.

The death penalty on the emigration of Venetian glass-blowers did not prevent their art from filtering out into other countries in the sixteenth and seventeenth centuries. The Venetian Gridolphi, who came to work in the Netherlands, complained that



Fig. 9. Glass workshop from the year 1550, a contemporary print by Georg Agricola, *De re metallica*, Basle 1556.

the local glassware was hardly to be distinguished from genuine Venetian ware. In 1575 Verzelini acquired a 21-year monopoly in England for making "Venetian glass", on condition that he taught the English the art. In 1592 he sold his patent to English merchants, who were able to extend it for seventy years.

Meanwhile glass had come into use on a large scale for household ware, for chemical equipment and other appliances, and for window panes. The large glass furnaces illustrated by Agricola in his "*De re metallica*" (1556) provide evidence of the volume of this production (fig. 9). The Italian scientific achievements of 1550-1650, to which we shall return presently, owed a debt to the Venetian art of glass-blowing. The fact that the alchemists were also keenly interested in glass is not surprising. They had a special symbol for glass (fig. 10), as they had for other important substances. As early as about 550 A.D. Aeneas of Gaza remarked that the emergence of the brilliant substance glass from the fusion of humble, almost worthless raw materials was an example of the "metamorphosis of matter into a

³⁾ Hrabanus Maurus, *De originibus rerum*, Monte Cassino mss. 1023.

⁴⁾ *Compositiones Variae*, Codex 490, Bibliotheca Capitularis, Lucca; Heraclius, *über die Farben und Künste der Römer*, Edit. Ilg, Vienna 1873; W. Theobald, *Des Theophilus Presbyter Diversarum artium schedula*, V.D.I. Verlag, Berlin 1933.

superior state", which was the avowed object of the alchemists. In the technology of glass, however, their efforts brought little progress, owing to the lack of essential knowledge of its composition.



Fig. 10. The alchemists' sign for glass, composed of the symbol X for breaking, the sign ♀ for Mercury and the sign / indicating a blowpipe plus bulb. (After K. F. Bauer, *Glastechn. Berichte* 24, 191, 1951.)

The 17th century ushered in important changes. The year 1612 saw the publication of Neri's hand-book which, soon translated into many languages, disclosed the Italian art of glass-making to the glass-blowers of other countries⁵). In 1615 the shortage of timber for the English Navy became so acute that glass-makers and others in England were forbidden to use timber as fuel. This prohibition had long been threatening, and patents had already been granted for the smelting of glass in crucibles in a coal furnace, using "sea-coal" from Newcastle. After many experiments, Ravenscroft succeeded in making a softer and more brilliant glass than the Venetian soda-lime product (1675). His potash lead-oxide glass could be made entirely from native English materials. It was marketed by the Glass Sellers' Company, and also enjoyed considerable success on the continent of Europe. In Holland, Anna Roemer Visscher, in the first half of the seventeenth century, had created a vogue for dot-engraved drinking glasses ("rummers", see *fig. 11*) which now, in about 1700, were made from the new "crystal glass".

Meanwhile in Bohemia and Germany a potash-lime "crystal glass" had come into use. Kunkel describes how much better this could be worked on a rotary grindstone than soda-lime glass, a method introduced by Caspar Lehman, jeweller at the court of Rudolph II. At the same period opaque glass was made with the aid of stannic oxide and calcinated bone or horn, and in about 1675 gold-ruby glass was made from "purple of Cassius", a compound of stannic chloride and gold chloride. The Bohemian crystal caused a decline in the Venetian glass industry, but was overshadowed in its turn by the English crystal towards the end of the eighteenth century.

⁵) Antonio Neri, *L'arte vetreria*, Florence 1612.
 English: C. Merret, *The art of glass*, London 1662.
 The art of glass by Mr. H. Blancourt, London 1699.
 Latin: *De arte vitraria Libri VII*, Amsterdam 1686.
 German: J. Kunkel, *Ars vitraria experimentalis*, Amsterdam and Danzig 1679.
 French: M. D., *Art de la verrerie*, Paris 1752 (annotated by Merret and Kunkel).
 J. Haudiquet de Blancourt, *De l'art de la verrerie*, Paris 1697.

In France, Jean Baptiste Colbert, Minister of the Crown under Louis XIV, set out to make the native glass industry independent of Venice by protective legislation. The factories at Baccarat, Clichy and St. Louis were soon turning out millefiori work and mirror glass of excellent quality, and in the middle of the nineteenth century French crystal glass gained the ascendancy, since heavy taxes, which were not lifted until 1845, now encumbered the English glass industry, which indeed had partly



Fig. 11. Dutch drinking glass from 1621, ornamented with diamond engraving by Anna Roemer Visscher. (Courtesy of Rijksmuseum, Amsterdam, and the Stichting Openbaar Kunstbezit.)

crossed over to Ireland. Nevertheless, it remained inventive. Discoveries made at that time were that good opaque glass could be made with arsenic compounds and that the addition of blast-furnace slag represented a saving in alkali; in 1755, a transparent ruby-lead glass was invented.

The early development of the American glass industry was beset with difficulties. Attempts made

by the London Glass Company in 1608 and 1621 to start manufacturing glass in America ended in failure. Brief successes in the eighteenth century were strangled by the competition from the mother country. It was not until after 1820 that a series of improvements were introduced into the manufacture of glass in the New World which were gradually to promote the American glass industry to a position of pre-eminence. The first of these improvements was the mechanical pressing of glassware in iron moulds, a process invented in 1827 and employed by the Boston and Sandwich Glass Company; further developments will be discussed in another context.

After this more general survey of the history of the glass industry, we shall now consider in somewhat more detail the evolution of various applications.

Glass crucibles and vessels

In the Middle Ages, scholars like Robert Grosseteste (1175-1253) were already using glass in their laboratories for reaction vessels, crucibles and retorts, glass having the obvious advantage of enabling the experimenter to see what was taking place

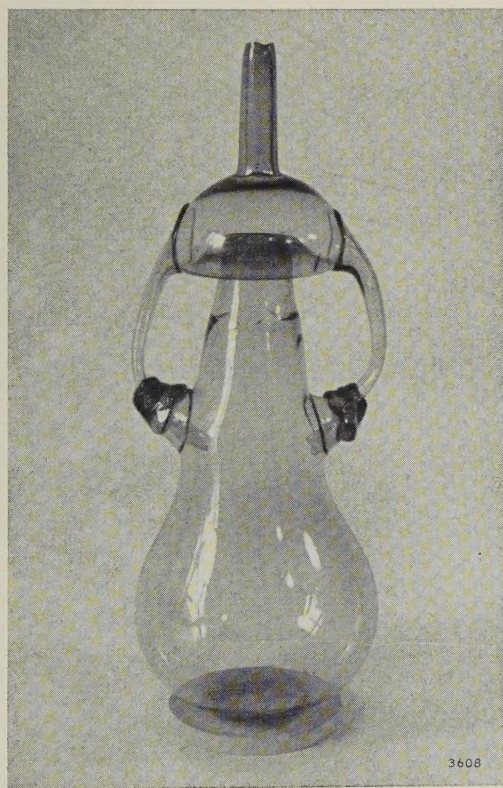


Fig. 12. Seventeenth-century "pelican" retort. An account of such retorts is given e.g. by E. J. Holmyard, *Alchemy*, Penguin, London 1957. The fine example shown here has become known as "Rebecca with the pitcher". (Courtesy of Rijksmuseum voor Geschiedenis der Natuurwetenschappen, Leyden.)

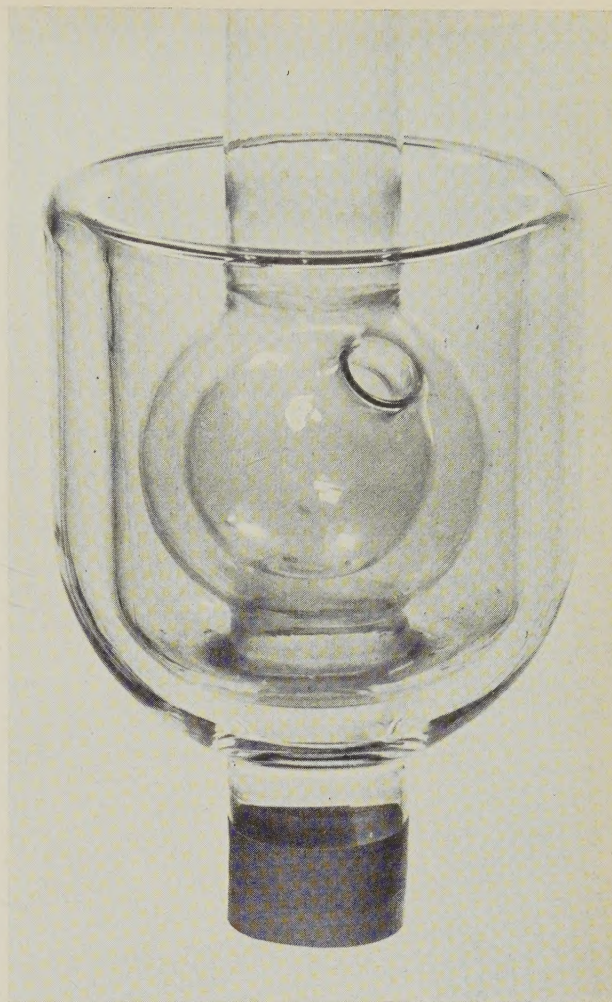


Fig. 13. Liquid-air-cooled vapour trap of very high conductance and high condensation efficiency, for an ultra-high vacuum pump built at Eindhoven (A. Venema and M. Bandringa, *Philips tech. Rev.* **20**, 151, 1958/59). The vessel is filled by pouring liquid nitrogen (e.g.) into the "beaker"; the liquid then also enters and fills up the innermost bulb.

inside the vessel. Generally, however, the early glass was not well able to withstand the protracted heating which was then an important aspect of chemical research. To make the glass vessels heat-resistant they had to be given a clay jacket, which of course destroyed the advantage just mentioned. Moreover, the glass was not well able to withstand leaching. Boerhaave (1668-1738) devoted a special treatise to the proposition that the protracted boiling of water in a glass retort would produce "earth"; this proved to be leached constituents of the glass wall⁶). Fig. 12 shows a 17th century distilling vessel of the "pelican" type, much used by Boerhaave. Better glass for chemical equipment first appeared after the foundation of the Schott factory at Jena (1882). The borosilicate glass "Pyrex", now very

⁶) H. Boerhaave, *Elementa Chemiae*, Leyden 1731/32; see also A. S. Margraf, *Mém. Berl. Akad. Wiss.* 1766, pp. 20-31, where Boerhaave's hypothesis is disputed.

widely used, was developed in about 1910 by the Corning Glass Works in New York state, and was first marketed in 1915. The refinement of glass-blowing techniques and the Moissan electric furnace (1893) also made it possible to process quartz for making laboratory appliances (1904). Interchange-

illustrated in *fig. 13*. Particularly impressive are the large apparatus for the chemical processing of liquids which must not come into contact with metals: even the pumps in such equipment may be made entirely of a special type of glass ("Duran", Schott).



Fig. 14. Part of a painting (c. 1450) by Rogier van der Weijden, showing the Saints Cosmas and Damianus, patron saints of medicine (and also, because of the correspondence in name, of the Medici family at Florence, who very probably commissioned the painting). The Saint in the centre holds in his hand a urine glass. Doctors at that time were particularly preoccupied with uroscopy. (Courtesy of Städelches Kunstinstitut, Frankfurt am Main.)

able ground glass joints (1929) and ground glass stoppers (1918) greatly facilitated the construction of chemical equipment, and introduced glass where metal had previously been used. Modern laboratory glassware may sometimes assume intricate shapes, as

Glass was more easily turned to use for medical purposes than for chemical processes. The inspection of urine for colour and sediment in the transparent, appropriately shaped urine glass (*fig. 14*) played an important part in mediaeval medicine,

even though it was later officially banned as a diagnostic method owing to its abuse by quacksalvers. Again, transparency and easy shaping (shapes were at first rather complicated) were the principal requirements for the thermometer, since c. 1610 an important medical instrument, which was introduced into general clinical practice by Boerhaave 100 years later (*fig. 15*). In 1584 Jeremias Martius wrote: "Das Glas braucht der Mensch auf mancherlei Weg, aber der Nutz, so es in der Artzney hat, übertrifft das ander alles" ("Man uses glass in many ways, but nowhere is it more useful than in medicine").

Windows

The dwelling house of Antiquity, with its inner courtyard and few windows, had little need of glass window panes. The coverings used were lattices of wood or earthenware, slabs of translucent selenite or alabaster, or oil-impregnated bladders and sheets of parchment. The first glass window panes were found in excavations at Pompeii, in particular in a building dating from about 60 B.C. These were cast on a flat stone or in a mould and drawn on all sides with pincers (as described by Theophilus) to an average size of 1' x 2'. There were also round glass disks measuring 2 to 2½' in diameter, and mounted in a marble frame. In the Eastern Roman Empire blown disks 6 to 8" in diameter first appear in the fourth century; these seem to be the forerunners of the Norman "crown glass", which was made in the Middle Ages in the West. The process applied was to take a blob of glass from the blowpipe on to a "pontil" (an iron rod) and to rotate it rapidly until it flattened into a disk thicker in the middle than at the edges (*fig. 16*). Panes made in this way were still in use up to the nineteenth century.

Another method, also described by Theophilus⁴⁾, produced what was known as "broad glass". By this method, developed in Germany, a cylinder was blown to a length of 4 to 6' and a diameter of 1 to 2'; both ends were removed and the cylinder was cut open while hot and rolled flat on a stone table with the aid of a piece of wood, after which the pane was cooled in a kiln. Excellent results were obtained with this process. In 1832 it was imported from France to England, where it was further developed. The Chance Brothers Glass Company succeeded in making cylinders 6' in length and 1½' in diameter, and a better method of abrasion and polishing was discovered. It was in this way that the panes were made for the Crystal Palace in 1851, thus marking the advent of glass as a *structural material*. The same year saw the similar use of glass for building a large hothouse, in which the exotic Victoria Regia



Fig. 15. One of the earliest sealed liquid-thermometers, built by Santorio at Florence in about 1650 for meteorological and medical work by the Accademia del Cimento. These thermometers were filled with alcohol ("acqua arzenite bianca") and the scale graduation — usually in 100 or 50, but sometimes in 300 or even 520 "degrees" — was marked with enamel beads: black for the digits, white for the tens and blue for the hundreds. A recent calibration has shown that the inside diameter of the metres-long stem (here wound in a spiral, though straight types also exist) is remarkably constant. (Courtesy of Museo di Storia della Scienza, Florence. See also: M. L. Bonelli, *Gli strumenti superstiti dell'Accademia del Cimento*, Domus Galil., Pisa 1958.)

was made to bloom for the first time in Europe. (The hothouse, although in more modest dimensions, already existed in Roman times, pumpkins being grown for Tiberius Caesar in a box closed with "transparent stone" to protect them from inclement weather.) The cylinder method reached its highest stage of development when Lubbers in 1903 succeeded in drawing (whilst blowing) cylinders 40' long and 3' in diameter from a crucible in the furnace.

Glass panes of greater mechanical strength and also, after somewhat cumbersome working, of superior quality were produced by a casting process.

This process received considerable impetus, particularly in France, from the demand for mirrors and for carriage-door windows. In about 1690 the cast-glass process underwent considerable improvement at the Royal glass factories at St. Gobain. The molten glass was poured on to a metal table and flattened with rollers, after which the glass plate was ground and polished. Blessed with abundant

Bessemer attempted in 1846 to cast glass from the furnace through two rollers, but it was not yet possible to make this into a continuous process. In 1884 the Chance Brothers evolved a method of casting glass on to a sloping plate and subsequently rolling it. In 1857 a patent was granted on a process of drawing plate glass from a furnace, but it was not until 1901 that Fourcault was able to apply

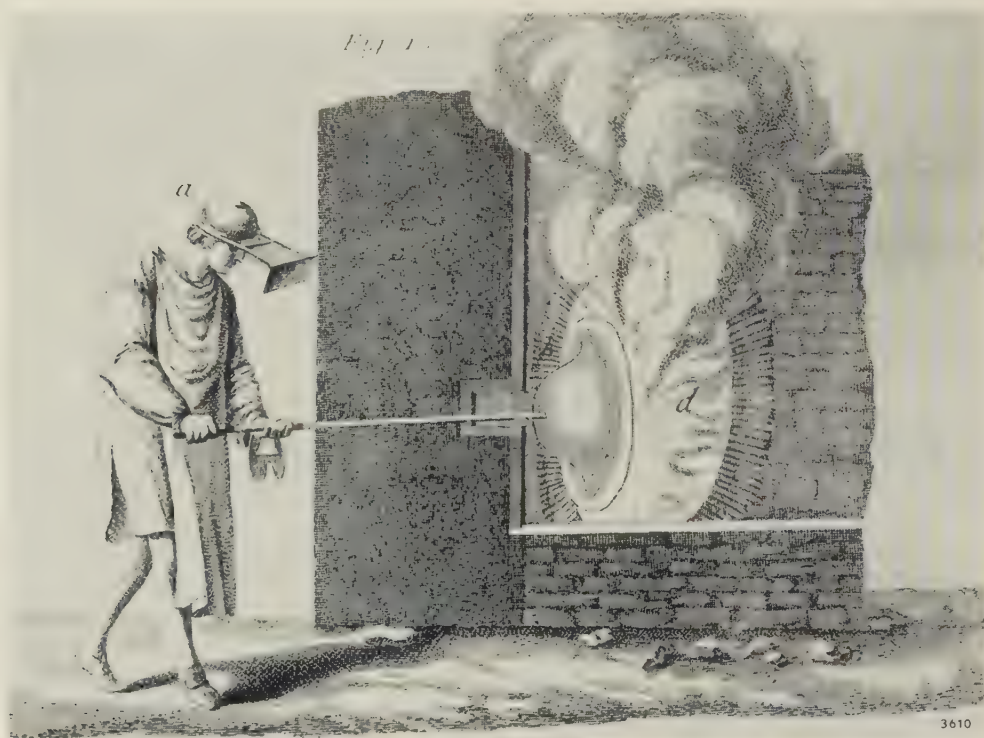


Fig. 16. Crown glass being made with the "pontil" (a solid iron rod). A gather of glass from the furnace is first blown into a sphere. This is taken over with a pontil, diametrically opposite the blowpipe. By renewed heating of the now opened sphere in the furnace and rapid rotation of the pontil, the glass is flattened into a disk having a thicker part in the centre (the "crown"). The glass workers wore protective masks during this very hot and rather hazardous process. (From "Encyclopédie ou dictionnaire raisonné des sciences, des arts et des métiers" by Diderot and d'Alembert, Paris 1752-1777; in part re-issued by Dover, New York 1959.)

supplies of timber for fuel, the industry flourished in France.

Not so in England. Although the casting process had been imported there in 1670 for the manufacture of window panes, the economy of production was hampered by a tax on window space. In 1773, French skill in this field was brought to England by the Huguenots, and in 1776 the Ravenhead glassworks managed to cast panes measuring 12' × 6'. Through the use of a cast-iron base plate the dimensions were increased in 1843 to 15' × 9'. The growth of building activity in England around 1820 stimulated efforts to find better and preferably continuous methods of producing window glass.

this process by drawing glass from the furnace under hydrostatic pressure through a slit, the "débiteuse" and then rolling it. This had become a commercial process by 1913.

Mirrors

The earliest mirrors were of metal (bronze or silver), although the Egyptians also used mirrors of opaque black glass. Glass mirrors, with a backing of tin foil, first appeared in about 200 A.D. Mediaeval mirrors were usually octagonal, slightly convex pieces of glass, backed with lead. In 1503 the Del Gallo brothers invented the method of treating the back of mirror glass with a tin-amalgam, for which

they were granted a 20 years' patent in 1507. The method of applying a backing of silver to glass by chemical means was not discovered until about 1840. (Silver has now been almost entirely supplanted for this purpose by aluminium.) The size of mirrors, like the subdivision of windows, was governed by the attainable size of the glass plate. To make such mirrors really flat was very difficult, as anyone can see who walks around a hall of mirrors of the Rococo period: up to the end of the eighteenth century, large mirrors were still built up from small sections.

Stained-glass windows

The use of glass for church windows is mentioned in documents dating from the fifth century; coloured church glass was first reported by Anastasius in about 800. This application of coloured glass seems to have been evolved in Constantinople from the ancient Egyptian art of glass mosaics. Instructions for making leaded glass windows are given by Theophilus ⁴) and other writers. Like the ancients, mediaeval craftsmen made blue glass with copper salts, green with iron and copper, dark-blue to purple with manganese, red opaque glass with cuprous oxide, white opaque glass with stannic oxide, yellow opaque glass with antimonite oxide, and black glass with a great deal of iron, copper or manganese. The fourteenth century discovered the art of producing lemon-yellow and orange coloured glass with silver chloride. Neri ⁵) gives recipes for dark-blue cobalt glass.

The coloured glass was cut into pieces following the outlines of drawings; up to about 1500 this was done with a hot iron, after which time diamond began to be used. The pieces were joined together with strips of lead to form a window. The earliest stained-glass windows were built up in this way from simple pieces of coloured glass. In the 13th century the practice started of painting the coloured glass with "grisaille" (glass frit, powdered metal and gum), which was baked in to produce shading effects (*fig. 17*). In the 16th century, grisaille and enamel paints were applied directly to colourless panes, thereby degenerating the stained-glass window to an imitation of the art of panel painting.

The great advances in chemistry between 1750 and 1850 made it possible to produce types of glass in many new colours ⁷), which were now not only used for artistic purposes, in leaded windows or for ornamental glass, but also for more everyday uses in all kinds of household glassware. In 1774



Fig. 17. Part of a stained-glass window dating from 1220, originally in Gery Abbey, demolished at the end of the 18th century, and now in the Musée de Cluny, Paris. The panel shows St. Martin arriving at the gate of Amiens, where he gives a beggar half his mantle, which he cuts through with his sword. The lead strips holding the pieces of coloured glass are seen to be an integral part of the composition, e.g. in the contours of horse and sword. (Reproduced with the cooperation of N.V. Filmfabriek Polygoon, Hilversum.)

it was found that nickel salts (discovered in 1751) produced glass ranging in colour from brown or grey to purple, and in 1779 that ferric oxides gave a blue glass and uranium salts a yellow glass. Green chrome-glass was discovered round about the same time. Thénard (1777-1857) made a systematic investigation of the influence of added salts. The purer substances of the new chemical technology made it possible to obtain better reproducible colours.

In the foregoing we have outlined the evolution which glass has undergone under the impact of practical requirements and the possibilities opened up by the advance of chemistry, an evolution which clearly demonstrates the cooperation that has grown up between glass-maker and natural scientist since the Renaissance. The finest example of this cooperation, however, is to be found in the history of spectacles, the telescope and the microscope.

"Roundels for the eyes"

Lenses for use as burning-glasses were already known in Antiquity. Strepiades, a character in Aristophanes' "Clouds", says that a burning glass, for lighting a fire, might also be used for setting a Court Order alight from a distance without touching it. It is probable that lenses were used as primitive magnifying glasses by the cutters of gems and cameos. Science in Ancient Greece was acquainted with katoptrics, the theory of reflection from mirrors, etc., and also with dioptrics, the theory of the

⁷) W. Ganzemüller, Beiträge zur Geschichte der Technologie und der Alchemie, Chemie-Verlag, Weinheim 1956.

refraction of light. The astronomer Ptolemy even gives a table of angles of incidence with their associated angles of refraction, without attempting, however, to give laws for the relation between them. Hellenic scientists also studied the rainbow and the functioning of the eye, both of them problems concerning the refraction of light.

The Greek heritage was preserved and further developed by Arabian scholars, notably by Ibn-al-Haitham (965-1039), known in the Middle Ages as Alhacen, whose "Opticae Thesaurus" served as the basis of all theories on the operation of the eye, mirrors, etc. right up to the seventeenth century (fig. 18). To make it more accessible to European scholars, his work on the rainbow was translated into Latin in 1170, and his "Opticae" in 1269. At

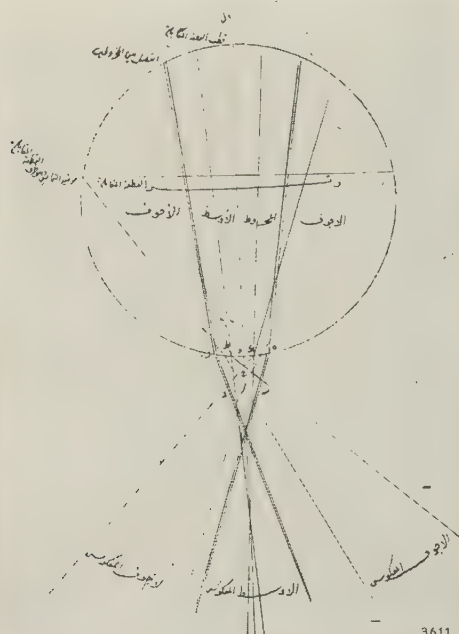


Fig. 18. Drawing by Ibn-al-Haitham (Alhacen, early 11th century) of the way in which a crystal sphere projects an image. The drawing is reproduced from a copy of the commentary written by Kamâl al Dîn in about 1310 on Alhacen's "Opticae". From the book it is evident that Alhacen knew that only the rays close to the optical axis must be used to produce a sharp focus. (Courtesy of the University Library, Leyden.)

about this time various scholars in the West, amongst them Robert Grosseteste and Roger Bacon (1214-1294), began to take an interest in optics. Grosseteste proposed the use of lenses for magnifying small objects and bringing distant objects closer. Bacon suggested that the focus of the eye in long-sightedness due to old age might be corrected by using a segment of a sphere of glass. Soon afterwards the first spectacles appeared, although they were not yet designed and constructed on scientific principles (fig. 19). They were probably invented round about

1280; in his book on wine, brought out in that year, Arnald de Villanova mentions a "euphrasia", a wine that makes the eyes brighter and helps people "to read small print again without eye glasses". The Venetian regulations for "cristalerii" (glass-blowers) of 1300 also make reference to "roidi dagli" ("roundels for the eyes"). In the fourteenth century they were being made in Flanders and Zeeland (Holland), and later in Bavaria in the towns of Nuremberg, Augsburg and Regensburg. Concave lenses for short-sightedness were first mentioned by Nicolaus of Cusa, in about 1450, and first illustrated in 1518. Until Kepler explained the action of eye and spectacles in his textbook on optics (*Ad Vitellionem paralipomena*, 1604), spectacles were made on a purely empirical basis, although the demand for them had greatly increased after the invention of printing. In the seventeenth century, spectacles were already in common use, but it was not until a century later that physicians began to study optics seriously. Bifocals, i.e. spectacle lenses of two powers, one for distant vision and the other for reading, were made by Franklin in 1760. Cylindrical lenses for correcting astigmatism were designed by Young in 1800, and introduced into Holland by Donders in 1864. By the nineteenth century, empiricism had been so far routed that people now began to consult an eye specialist before buying spectacles. In 1890 Von Rohr computed the famous "Punktal" lens for Zeiss. Subsequent developments with regard to spectacles are more a question of fashion than of science.

Glass reveals new worlds

Before the appearance of Kepler's treatise on optics Zacharias Jansen of Middelburg, Netherlands, had already made a telescope, in about 1590, consisting of a double-convex objective lens and a double-concave lens as eye-piece. In 1620 he made a binocular telescope for Prince Maurits of Orange. At about the same time telescopes were also being made in Italy. Galilei, inspired by an instrument imported from Holland, made a telescope himself in 1609, with which he observed details of the surface of the moon, the satellites of Jupiter, the phases of Venus and the spots on the sun — discoveries which he described in his "Nuncius Sidereus" of 1610.

The earliest microscopes appeared in about 1620. In 1667 Robert Hooke published his "Micrographia", but his lens systems were weaker than the single lenses ground from small glass spheres by Anthonie van Leeuwenhoek, with some of which magnifications of more than 200 times were achieved! Unfortunately, Van Leeuwenhoek never

disclosed the methods he used to grind his excellent lenses.

The mathematical theory underlying the design of optical systems and lenses, and the theories of light on which the optical laws could be based, were created in the seventeenth century. Descartes, who laid the foundations of analytical geometry, of great importance to optics, provided in his "Dioptrique" (published as a supplement to his "Discours de la Méthode", Leyden 1638) a mathematical derivation of Snell's law of refraction (1621). In 1665 Grimaldi published a treatise on the reflection, refraction and diffraction of light. Christiaan Huygens, who himself made lenses together with his brother Constantijn Huygens (figs. 20 and 21), expounded his wave theory of light in "Dioptrica", a work otherwise concerned entirely with geometrical optics, on which he worked from 1652 to 1692. Newton's emission theory was put forward in his "Opticks" of 1704.

The lenses used by these workers had largely to be made by themselves. Good instrument makers, like Eustachio Divini (1620-1695, in Italy) and Christopher Cock (1660-1696, in London) were few and far between. Soon, however, determined efforts were made to overcome the defects of lenses arising from shortcomings in the glass as well as from the intrinsic errors such as spherical aberration, distortion, astigmatism and chromatic aberration. In his "Géométrie" Descartes had already shown that spherical aberration might be corrected by using lenses with elliptical and hyperbolic surfaces, but the grinding machines at that time were not capable of producing such surfaces⁸). Use had therefore to be made of lenses of considerable focal length, in which the error was not so noticeable. As regards chromatic aberration, Newton believed that this was not to be avoided, but Klingenstierna at Uppsala calculated in 1760 that the solution could be found in a combination of convex and concave



Photo Ohmeyer

Fig. 19. Part of a painting by Friedrich Herlin (Circumcision of Christ) dating from 1466, on an altar in St. Jakobs Kirche at Rothenburg ob der Tauber, showing a man wearing spectacles. On the Predella of the same altar the painter also represents a bespectacled Peter the Apostle. The spectacles in both cases are of the "hinged" type, having exactly the same form as depicted more than a hundred years earlier (1352) by Tommaso Barisino in a fresco at Treviso. (Courtesy of the custodian of St. Jakobs Kirche, Rothenburg, Germany.)

lenses of different types of glass, i.e. of different refractive index. Chester Moor Hall in 1733 had meanwhile arrived at the same conclusion empirically, and John Dollond, an instrument maker, was granted a patent for achromatic lens combinations of this sort in 1758. He put them on the market, but it was not until about seventy years later that they found general application in microscopes.

The shortcomings in the glass itself were mainly poor surfaces and inhomogeneities, and we shall now consider the efforts made to overcome them. Like the application of types of glass with specific optical properties, they provide another striking illustration of the fruitful exchange between the natural sciences and the glass industry.

⁸) C. A. Crommelin, *Het lenzen slijpen in de 17de eeuw*, H. J. Paris, Amsterdam 1929. (The grinding of lenses in the 17th century; in Dutch.)

for example, had been marketed since 1790 — and these gradually supplanted the impure natural products.

Only with the improved quality of lenses did it become possible to derive full benefit from achromatic objective lenses for microscopes, and the years between 1830 and 1880 saw a rich harvest of biological and medical discoveries. In the same period, too, there was a spate of new optical instruments. The following summary of the more important of these instruments will help to show their significance to science and industry:

- 1) The polarimeter, created by Nicol (1833, 1840), and improved by Savart and others.
- 2) Associated herewith, the Biot saccharimeter (1842), which evolved through a succession of improvements to its final form in 1874.
- 3) The primitive refractometer invented by the Duc de Chaulnes (1767) was made into a precision instrument by Abbe (1872).
- 4) The interference equipment of Fresnel (1822), Brewster (1831) and others evolved into the modern interferometer — the Fabry and Pérot interferometer (1899) and that of Lummer and Gehrcke (1901).
- 5) The spectroscope, introduced as a laboratory instrument by Meyerstein (1856), was used by Bunsen and Kirchhoff for chemical analysis (1861).

Once again, we see the repercussions of this development on the glass industry. In 1876, Abbe and Von Helmholtz pointed out that the usefulness of optical instruments depended not only on the quality of the lenses and prisms, but also on the optical properties of the glass used. Schott, who had been looking for new types of glass with better properties, entered into cooperation in 1884 with Abbe and with Carl and Roderich Zeiss at the glass-works at Jena. At that time the optical properties of only some ten types of glass were known; within a few years they had tested thirty new elements as supplements or substitutes for the old range of seven elements used in the manufacture of glass. Schott's catalogue of 1902 offered no less than 80 types of optical glass.

Bottles and lamp glasses

Whilst the advances in chemistry were steadily placing the manufacture of glass on a firm scientific basis, and Abbe and Zeiss, working on a foundation of theory from preceding generations, were creating optical glass as we know it today, the glass industry also began to undergo radical changes in its methods of production. The nineteenth century, with the

beginnings of mass production, saw the introduction of *mechanization* into glass manufacture, as in so many other fields. Glass tubing and bottles, needed in such large quantities and for so many purposes, were obvious candidates for mechanization. Between 1859 and 1893, numerous semi-automatic machines for bottle-blowing were patented, the most successful of which was the machine invented by Ashley. The first completely automatic bottle-making machine was the work of Owens



Fig. 22. 12th century illumination of the initial letter L, from a *Passionale* (book on the sufferings of the Saints and Martyrs) originating from Hirsau Abbey. The priest Lucian, asleep in the baptistery, receives instructions from Gamaliel on finding the remains of the martyred St. Steven (415 A.D.). Above the sleeper is depicted a lamp enclosed in glass. (Courtesy of Landesbibliothek Stuttgart; see also: K. Löffler, *Schwäbische Buchmalerei in romanischer Zeit*, Augsburg 1928.)

in America, who in 1898 designed his "hand-gun" for gathering from the furnace the right amount of glass to be blown into a bottle. Together with Libby, Owens built between 1899 and 1904 a completely automatic bottle-making machine with six to fifteen arms, capable of turning out hundreds of bottles an hour⁹⁾.

The use of glass for lamps was already known in Antiquity; the word "candela", now part of the lighting engineer's vocabulary in another sense,

⁹⁾ W. C. Scoville, *Revolution in glass-making 1880-1920*, Harvard Univ. Press, Cambridge 1948.

originally meant a glass oil lamp. At first, glass simply replaced the ceramic material formerly used for holding the oil. In about the seventh century A.D., however, it is recorded that oil lamps or candles in portable "lanterns" began to be enclosed in transparent glass to shield them from the wind. This use of glass as a "container" for a light is to be seen in many mediaeval drawings (*fig. 22*). Early in the nineteenth century, lamp glass began to be mass-produced for the chimneys of the new lamps burning oil, kerosene or colza oil. In 1785 Argand had to go to England to find glass-blowers able to make lamp glasses, but by about 1840 they were being produced all over Europe, and the market was further expanded after the invention of the incandescent gas mantle in 1883. This production,

too, was mechanized in about 1900. The Schott Works at Jena, which employed their new refractory borosilicate glass for this product and turned out some 40 million lamp glasses a year, owed much of their prosperity and growth to this production.

In 1879 the Corning Glass Works made glass bulbs for Edison, who brought out his first incandescent electric lamps two years later (*fig. 23*). From that modest beginning arose the electric-lamp industry. Its elaborate bulb-blowing machines now produce thousands or tens of thousands of bulbs an hour¹⁰). The process somewhat resembles the automatic manufacture of bottles — for which reason bottles and lamp glass are here lumped together under the same heading.

The last fifty years have witnessed the birth of so many new applications of glass that our relatively detailed account must end at this point. The manufacture and use of glass in the present century are dominated by the influence of scientific investigation. Chemical research led to the comparative analysis of silicates in general and to a deeper insight into the vitreous state. Physical research was no longer confined to the optical properties of glass. Interest began to be taken in its viscosity and thermal properties, such as its expansion, which are important in the glass-to-metal seals found in electric lamps and in so many instruments and apparatus. The investigation of its electrical properties led to the use of glass insulators in electrical equipment. Knowledge of its mechanical properties made glass into a modern structural material, and the study of its transmission of heat and light



Fig. 23. Some incandescent electric lamps from a collection of the Teyler Foundation. The lamps were bought in 1881 at the Paris exhibition of electro-technology. The whole collection comprises 20 lamps, made by Edison, Swan, Lane Fox and Siemens. (Courtesy of Teyler's Museum, Haarlem, Holland.)

¹⁰) See the article by P. van Zonneveld in this issue.

opened up the possibility of using glass as a heat insulator in buildings. Other developments were porous glass (frits), produced by sintering powdered glass, and glass "wool" and "textiles", made by the extrusion and spinning of fibres. These in turn led to fresh applications as a structural material (glass fibres for reinforcing polyesters, etc.) and, remarkably enough, to novel uses in optics (fibre optics¹¹). It is a fascinating study to follow in this way the evolution of glass from a crude substance used for

glazing the surface of pottery, or for making imitation jewellery, to one of man's most versatile materials with an ever-widening range of applications.

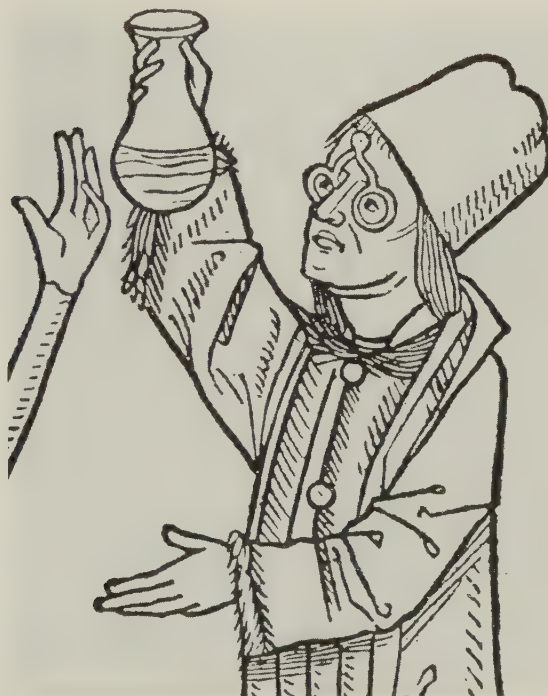
Bibliography (some books devoted to glass, which are generally available):

- R. Schmidt, *Das Glas*, Reimer, Berlin 1922.
 B. Kollak, *Glas, Technik und Kunst*, Winkler, Darmstadt 1937.
 O. Völckers, *Glas und Fenster*, Bauwelt-Verlag, Berlin 1939.
 W. B. Honey, *Glass*, Victoria and Albert Museum, London 1946.
 C. J. Phillips, *Glass the miracle maker*, Pitman, London 1948.
 W. Schnauk, *Glaslexikon*, Callwey, Munich 1959.

¹¹) See, for example, B. O'Brien, *Physics today* **13**, No. 1, 52, 1960.

Summary. The history of glass is surveyed up to about 1900, with special emphasis on applications. Glazing and glass-making techniques were used in Ancient Egypt and Mesopotamia, primarily for decorative purposes. The discovery of glass-blowing, in Phoenicia about 50 B.C., was soon followed by the quantity production of glass objects, including tableware, and by the spread of the glass industry into many parts of Europe. After briefly sketching the evolution of glass technology, touching on Arabian, Venetian and other products, the author devotes a series of short sections to the historical uses of glass for chem-

ical and medical purposes, for windows, mirrors and stained-glass windows, and for spectacles, telescopes and microscopes, leading up to the development of optical glass and the invention of many new optical instruments in the last century. An attempt is made throughout the article to show how the manufacture and uses of glass have gradually been placed on a more scientific foundation. Finally, the mechanization of bottle and lamp-bulb production is discussed. Only very brief mention is made of the many and varied new applications of glass in the last fifty years.



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Physician with spectacles and urine glass. Part of a woodcut from the Heidelberg Dance of Death, late 15th century.

NEW LIGHT ON THE STRUCTURE OF GLASS

by J. M. STEVELS.

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Introduction: Zachariasen's theory

The present-day conception of the structure of glass differs in several respects from that presented in Zachariasen's now classical work¹⁾. In order to explain certain physical properties of glass, the theory of the vitreous state has been modified and refined in various points, and in this article we shall deal with these changes under three main headings.

In each part we shall examine a separate aspect of glass structure. The first will be concerned with the coherence of the atoms in glass, and one of our conclusions is that the vitreous state can occur under other conditions than were formerly held to be possible. In the second part it is shown that glass is not the homogeneous and purely amorphous substance it was long thought to be. The last part deals with some new aspects of the structure of glass which stem from a concept of major importance in the physics of the crystalline state but which seems strange in relation to glass, namely the concept of lattice imperfections.

The better insight gained into the structure of glass has made many new applications possible, and has also led to the development of a category of glasses differing quite essentially from conventional types. Before considering the results of glass research in recent years, we shall briefly recapitulate Zachariasen's theory.

According to Zachariasen a substance in the vitreous state is built up of a random three-dimensional network which, in normal glasses composed of inorganic oxides, is constructed from polyhedra (tetrahedra or triangles) of oxygen ions. As a rule, the centres of the polyhedra are occupied by multiply-charged ions such as Si^{4+} , B^{3+} or P^{5+} ions. Since these form the network together with the oxygen ions, they are called *network formers*. The oxygen ions are of two kinds, known as *bridging oxygen ions*, each of which belongs to *two* polyhedra, and *non-bridging oxygen ions*, each of which belongs to only *one* polyhedron. The degree of cohesion between the polyhedra, and hence of the network as a whole,

evidently depends on the percentage of bridging oxygen ions. The excess negative charge of the network is compensated by *network-modifying ions*, located in the interstices of the network. These are generally large metal ions of low positive charge, such as Na^+ , K^+ or Ca^{++} ions. In conventional glasses they have little influence on the network compared with the network formers. Nevertheless, as their name suggests, they are not entirely to be disregarded.

A two-dimensional representation of the structure of an inorganic oxide glass in accordance with Zachariasen's theory is given in fig. 1.

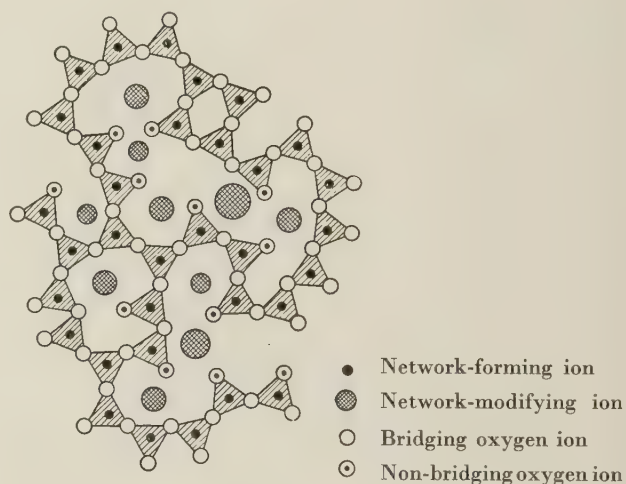


Fig. 1. Schematic two-dimensional representation of glass, according to Zachariasen's theory¹⁾.

The structure parameter Y and its influence on the properties of glass

To understand various physical properties of glass it is useful to introduce the following four quantities:

X = average number of non-bridging oxygen ions per polyhedron,

Y = average number of bridging oxygen ions per polyhedron,

Z = average total number of oxygen ions per polyhedron,

R = ratio of total number of oxygen ions to total number of network formers.

¹⁾ Zachariasen's theory and various hypotheses from the years 1940 to 1950 are discussed by J. M. Stevels in: The vitreous state, Philips tech. Rev. 8, 231-237, 1946, and in: The structure of glass, Philips tech. Rev. 13, 293-300, 1951/52.

Between these quantities two simple relations exist, which are easily found by counting the ions:

$$X + Y = Z, \quad (1)$$

$$X + \frac{1}{2}Y = R, \quad (2)$$

or

$$X = 2R - Z, \quad (3)$$

$$Y = 2Z - 2R. \quad (4)$$

As a rule the total number of oxygen ions per polyhedron Z is known ($Z = 4$ in phosphate and silicate glasses), and R can usually be calculated from the composition; it is therefore generally a simple matter to determine X and Y .

Given $Z = 4$ and $R = 2$ for quartz glass (i.e. fused silica, SiO_2), it follows that $X = 0$ and $Y = 4$. With $R = 3$ and $Z = 4$ for glass of formula $\text{Na}_2\text{O}.\text{SiO}_2$, we find $X = 2$ and $Y = 2$. Likewise, for glass having the composition $15\% \text{Na}_2\text{O} . 85\% \text{SiO}_2$ ($R = 1.85/0.85 = 2.175$ and $Z = 4$) we calculate $X = 0.35$ and $Y = 3.65$.

The situation is not always as simple as this. Some glasses contain ions which do not appear as typical network formers or network modifiers, but which occur both *in and between* the oxygen tetrahedra (or triangles). Where the "equilibrium" lies in such a case depends on the composition of the glass and on the conditions under which it was formed. It will be evident that the terms network former and network modifier are only appropriate in such a situation if the "equilibrium" lies in practically all circumstances completely to one side. When this is not so, the ions concerned, e.g. Co^{++} , Ni^{++} , Pb^{++} and in some cases Ca^{++} and Ba^{++} are referred to as "intermediates".

Where intermediates are present it is not generally possible to determine R exactly, since the situation of the "equilibrium" is not usually known. The practice is then to count the intermediates together with the network-modifying ions in the above formulae. Of course this means that the values of Y thus calculated (Y_c) will differ from the true values (Y_r), and it is not difficult to see that Y_c will turn out smaller than Y_r . An example of this will be given below.

Knowledge of the value of Y , the average number of bridging oxygen ions, is of considerable importance in view of the surprising fact that numerous properties of glass depend primarily on Y . Generally speaking, the spatial coherence of the network is less the smaller the value of Y : the structure becomes looser and this is accompanied by the appearance of larger interstices. As a result the network modifiers will be able to move more readily, both when oscillating in their own site and when jumping from one site to another through the meshes of the network. Thus, as Y decreases, we find an increasing coefficient of thermal expansion, an increasing electrical conductivity and a decreasing

viscosity, and analogous changes in various relaxation phenomena²⁾.

The influence of Y on various properties of glass appears from Table I. For each pair, the compositions of each of the vitreous systems mentioned are entirely different chemically, yet they have the same values of Y , and consequently almost the same physical properties.

Table I. Illustrating the influence of Y , the average number of bridging oxygen ions per polyhedron, on the "melting temperature" (temperature at which the viscosity reaches the value 10^2 poise) and on the expansion coefficient α of various glasses.

Composition	Y	"Melting temperature" °C	$\alpha \times 10^7$
$\text{Na}_2\text{O} . 2\text{SiO}_2$	3	1250	146
P_2O_5	3	1300	140
$\text{Na}_2\text{O} . \text{SiO}_2$	2	1050	220
$\text{Na}_2\text{O} . \text{P}_2\text{O}_5$	2	1100	220

Increasing the metal-oxide content of the glasses generally results in a lower Y , since the fusion of metal oxides and quartz glass gives rise to an Si-O network which differs from the quartz glass network in that at various places a bridging oxygen ion is replaced by two non-bridging oxygen ions. The extra oxygen needed for this substitution is supplied by the metal oxide. Plainly, then, more non-bridging oxygen ions will appear, and Y will become smaller the more metal oxide is used in forming the glass. This knowledge makes it possible — within certain limits — to give a glass the properties required for a particular purpose.

The boron anomaly

A higher metal-oxide content in glass does not *always* result in a lower Y . Pure borate glasses are a case in point. When not too large amounts of metal oxide and B_2O_3 are fused together, the oxygen of the metal oxide is not taken up as a non-bridging ion. This oxygen is taken into the network by the conversion of oxygen triangles into oxygen tetrahedra, which consist entirely of bridging oxygen ions.

This implies that raising the metal-oxide content of these glasses will entail an increase in Y , and thus strengthen the network. Correspondingly, various physical properties change in a direction exactly opposite to that in comparable silicate glasses under the same conditions. This is known as the "boron anomaly". It is customary to refer to the range of

²⁾ The latter are discussed by J. M. Stevels in: Dielectric losses in glass, Philips tech. Rev. **13**, 360-370, 1951/52.

compositions in which this effect occurs in borate glasses as the *accumulation region*.

The conversion, just mentioned, of oxygen triangles into oxygen tetrahedra is found to obey certain rules, which set a limit to the "accumulation"³⁾. These rules are:

- a) Each triangle must be associated with no more than one tetrahedron;
- b) A tetrahedron must not be associated with another tetrahedron.

This means that there must be at least four triangles present per tetrahedron.

If a borate glass contains more metal oxide than is consonant with this condition, non-bridging oxygen ions will be formed, just as in the case of silicate glasses: as a result, the value of Y will decrease as the metal oxide content increases. The range of concentrations where this occurs in borate glasses is known as the *destruction region*.

The effects described are well demonstrated by fig. 2: as the metal-oxide content increases, the coefficient of expansion α initially falls and then starts to rise again at a composition which exactly coincides with the point where the Y curve turns over.

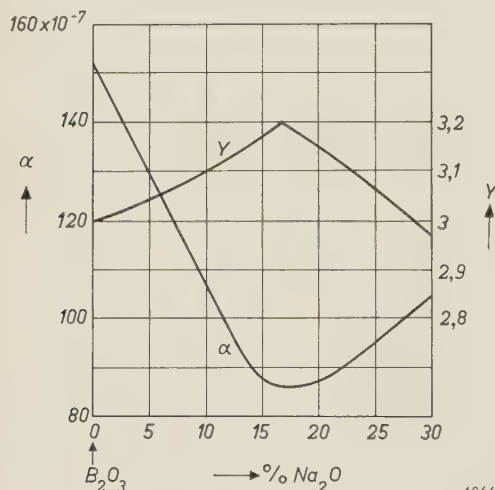


Fig. 2. Relation between Y , the average number of bridging oxygen ions per polyhedron, and the coefficient of expansion α of pure sodium borate glasses. Both quantities are plotted versus composition in mole % Na_2O . The structure with the largest value of Y has the smallest expansion coefficient.

The agreement between theory and practice in this connection will be made clearer by a few simple calculations. The theory leads us to expect the transition from the accumulation to the destruction region to take place at $Y = Z = 3.2$ and $X = 0$, since the network in the boundary case consists of polyhedra with three and four oxygen ions in the

ratio of 4 : 1, all of them bridging ions. For borate glasses the value $Y = 3.2$, according to the theory, indicates the maximum average number of bridging oxygen ions, and at this value the structure will thus be strongest. From eq. (2) - (4) it follows that the corresponding value of R is equal to 1.60 which, expressed in terms of chemical composition, corresponds to $\text{Na}_2\text{O} \cdot 0.5\text{B}_2\text{O}_3$, or 16.7% Na_2O . 83.3% B_2O_3 (mole percentages). Fig. 2 shows that the minimum of the expansion coefficient does in fact occur at exactly this value.

Changes where $Y = 3$

It is interesting to examine what happens when Y is equal to 3. It is understandable that when this value is reached — here, for *all* inorganic oxide glasses — marked changes may be expected, since polyhedra will now occur which are bound to their surroundings by only two points of contact. When this value is exceeded there will thus be a rather abrupt change in the stiffness of the network, and hence in the mobility of the network modifiers. The effects are apparent in various physical properties, as can be seen in figs. 3 and 4. These figures show the electrical conductivity of sodium silicate glasses and the Vickers hardness⁴⁾ of sodium borate glasses as a function of composition (and of Y). In the silicate glasses the value $Y = 3$ corresponds to the chemical formula $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ (33.3% Na_2O , 66.7% SiO_2), in the borate glasses to $2\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3$ (28.6% Na_2O , 71.4% B_2O_3). In both figures the curves show kinks at these compositions. Fig. 4 also shows the effect of the transition from accumulation to destruction region at 16.7% Na_2O .

Invert glasses⁵⁾

The changes that occur when Y is smaller than 2 are particularly important. The feature of the structures then produced is that the tetrahedrons have at the most two points of contact with their environment. In other words, the spatial coherence is lost, and the structure is built up from *chains*.

Disregarding the possibility of ring formation and branching, the chains are infinitely long in the case of $Y = 2$. A smaller Y implies a shorter chain. The average "chain length" \bar{n} , that is to say the average number of tetrahedra per chain, is given by:

$$\bar{n} = \frac{2}{2 - Y}, \text{ or } Y = 2 - \frac{2}{\bar{n}} \quad (5)$$

⁴⁾ On the measurement of the Vickers hardness of materials, see e.g. E. M. H. Lips, Philips tech. Rev. **2**, 179, 1937.

⁵⁾ For a detailed study of invert glasses, see H. J. L. Trap and J. M. Stevels, Glastechn. Ber. **32 K**, VI/31, 1959.

³⁾ T. Abe, J. Amer. Ceram. Soc. **35**, 284, 1952.

Y and \bar{n} can also be expressed in terms of chemical composition. For example, given a silicate glass of composition $(100 - p)\text{M}_2\text{O} \cdot p\text{SiO}_2$, where p represents the mole percentage and M is a general symbol for a monovalent network-modifying ion, then:

$$Y = 6 - \frac{200}{p}, \quad \dots \dots \dots (6)$$

or

$$\bar{n} = \frac{p}{100 - 2p} \cdot \dots \dots \dots (7)$$

It follows from these formulae that Y becomes smaller than 2 at less than 50 mole % SiO_2 and moreover that \bar{n} decreases very rapidly at percentages lower than this. At $p = 48$, for example, $\bar{n} = 12$; at $p = 45$, $\bar{n} = 4.5$; and at $p = 40$, \bar{n} is as low as 2. It is seen, then, that the properties of these glasses depend largely on composition — much more so than in the case of the conventional glasses earlier discussed.

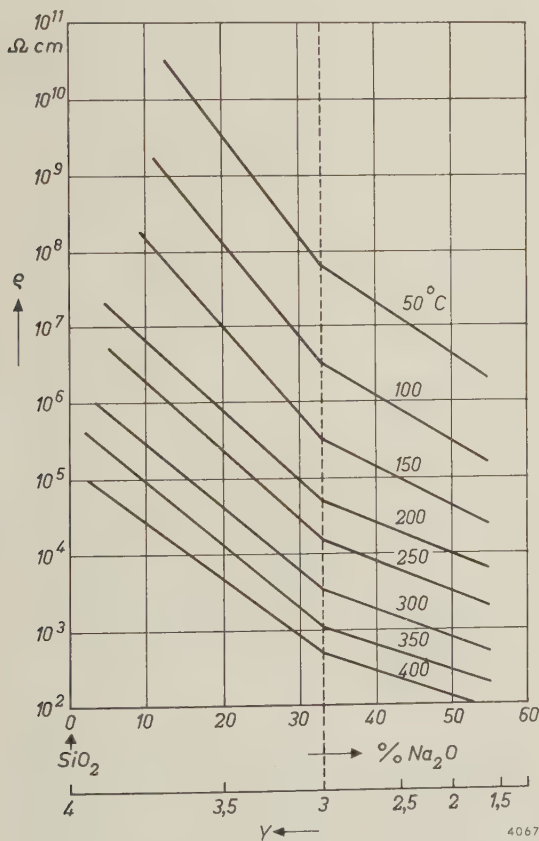


Fig. 3. Electrical conductivity ρ of sodium silicate glasses at various temperatures as a function of composition (in mole % Na_2O) and of Y . A value $Y < 3$ corresponds to the occurrence of tetrahedra bound to the rest of the network by only two bridging oxygen ions. At the value $Y = 3$ there occurs a discontinuous change in the "stiffness" of the network and hence also of the mobility of the network-modifying ions. This explains the kink in the curves. (After E. Seddon, E. J. Tippet and W. E. S. Turner, *J. Soc. Glass Technol.* **16**, 450, 1932.)

In practice it is very difficult to produce glasses in which $Y < 2$. In a system like $\text{Na}_2\text{O} \cdot \text{SiO}_2$, for instance, vitrification ceases entirely if the molar content in Na_2O exceeds 50%, the value that corresponds to $Y = 2$. This is bound up with the disintegration of the structure into chains and with the fact that the system contains only one kind of metal ion. Both these circumstances enable the metal ions together with the tetrahedron chains to assume an ordered arrangement when the melt solidifies, in other words, crystallization occurs.

This crystallization can be prevented by resorting to an artifice: if *two* kinds of metal ions are used,

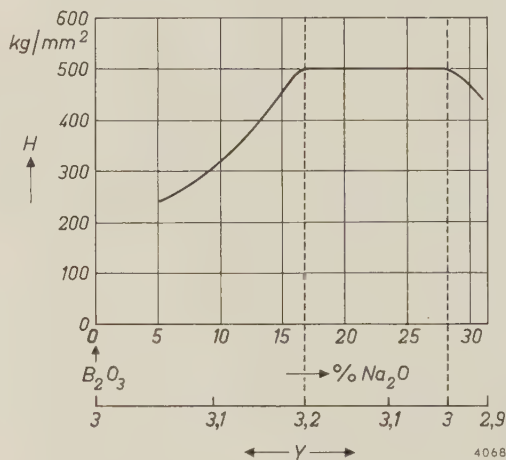


Fig. 4. The Vickers hardness H of sodium borate glasses as a function of composition in mole % Na_2O . Both the reversal point at $Y = 3.2$ (16.7% Na_2O) and the effect at $Y = 3$ (28.6% Na_2O) are perceptible in the curve. Compare also figs. 2 and 3. (After F. C. Eversteijn, J. M. Stevels and H. I. Waterman, *Phys. and Chem. Glasses* **1**, 134, 1960, No. 4.)

the vitreous region can be shifted to smaller values of Y , the idea being that crystallization is made more difficult when metal ions of *different size and charge* are present. By taking this principle far enough, e.g. by introducing four or five different metal ions into the same system, very low values of Y can be achieved⁶⁾.

The schematic representation of a glass in the region of $Y < 2$ is given in *fig. 5*. The average chain length is here 3.5, corresponding to $Y = 1\frac{3}{5}$.

Glasses in which $Y < 2$ have been called *invert glasses*, for two reasons. The first is that, compared with conventional glasses, their structure is in fact "inverted". The structural cohesion of conventional glasses is mainly due to the Si-O network, and the network modifiers play a subordinate part. In invert glasses exactly the opposite is the case. They con-

⁶⁾ This has not been investigated in the case of borate glasses.

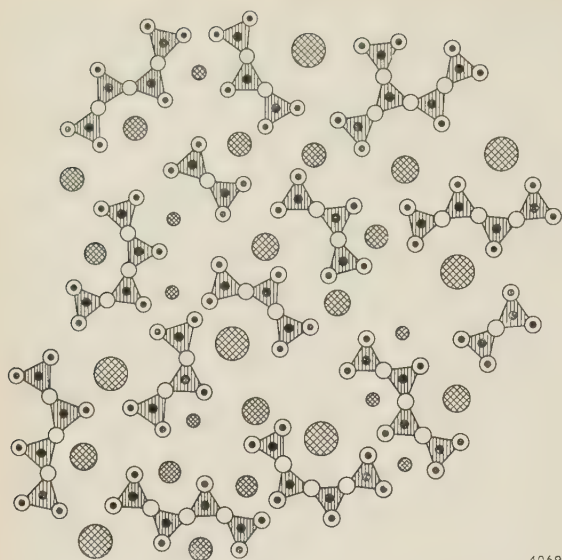


Fig. 5. Schematic two-dimensional representation of the invert glass structure. Compare with fig. 1, which explains the various circles. Instead of a coherent conglomerate of oxygen polyhedra with metal ions in the interstices, as in fig. 1, the oxygen polyhedra here form "islands" in a "sea" of metal ions. Such glasses can only be made by introducing metal ions of different size and charge to counteract crystallization.

tain only short chains of polyhedra which are embedded, as it were, in a large quantity of metal ions, and it is the forces between these metal ions and the oxygen ions of the chains that primarily determine the cohesion of the substance.

The second reason for the name "invert glasses" is that certain physical properties also exhibit an "inversion". We have seen that various properties of glasses change with decreasing Y in a way that corresponds to a decrease in the coherence of the structure. In the invert glass region the influence of the (short) chains of polyhedra is slight compared with that of the metal ions. The more the latter gain the ascendancy as Y decreases, the stronger the structure becomes, and certain physical properties undergo a corresponding change, i.e. in the opposite direction to that in conventional glasses. Of course, the properties in question are those which are primarily determined by the coherence in the structure, as for example the expansion coefficient, the viscosity and the dielectric losses.

As an example of this inversion, figs. 6 and 7 show the viscosity (at various temperatures) and the dielectric loss angle (for various mole fractions of the metal oxides) as functions of Y .

In a glass containing numerous intermediates the inversion occurs at a calculated value Y_c which is smaller than 2 (fig. 8), in agreement with the discussion in small print on page 301. In practice, this difference between the observed and theoretical values at which inversion occurs is often used for estimating the distribution of the intermediates into network formers and network modifiers.

Invert glasses have their practical as well as their theoretical importance. For example, in glass capacitors it is sometimes required that the capacitance suffers little change during switching; for this purpose glasses with a small temperature coefficient of the dielectric constant are required. Certain invert glasses are able to meet this requirement very satisfactorily in that their high dielectric constant and low dielectric losses are properties that favour the low temperature coefficient required.

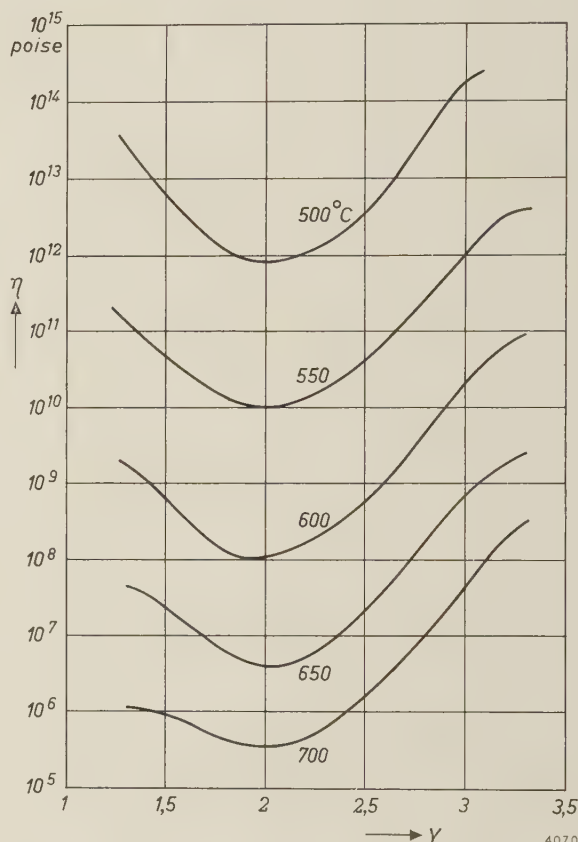


Fig. 6. Viscosity of $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{SrO}-\text{BaO}$ silicate glasses, at various temperatures, as a function of Y (equimolar quantities of the various metal oxides). The change in sign of the slope of the curves at $Y = 2$ is related to the fact that at $Y > 2$ the coherence of the structure is primarily determined by the Si-O network and at $Y < 2$ by the interaction between the metal ions and the oxygen ions of the chains.

For an explanation of this we refer the reader to an earlier article in this journal ⁷⁾. The effect of the structure inversion on the two properties mentioned can be seen in fig. 7 and fig. 9: the dielectric loss angle becomes smaller, whereas the dielectric constant increases monotonically. The latter is evidently not affected by the structure inversion, as this property does not depend on the coherence

⁷⁾ See e.g. M. Gevers and F. K. du Pré, Philips tech. Rev. **9**, 91, 1947/48.

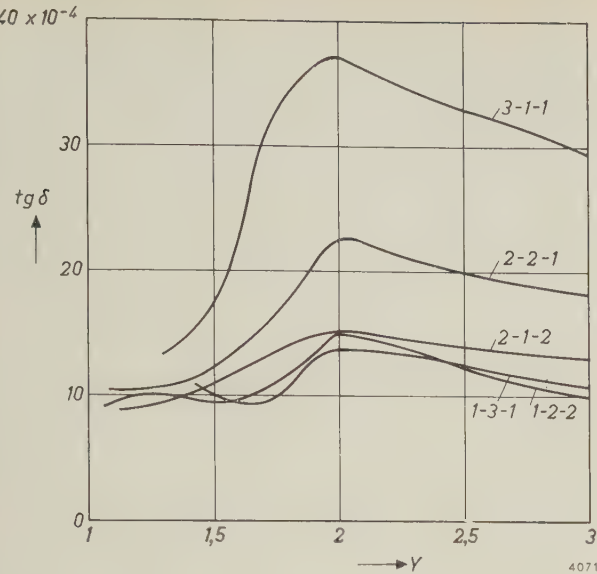


Fig. 7. The dielectric loss angle $\tan \delta$ of K_2O - CaO - SrO silicate glasses as a function of Y , measured at 1.5 Mc/s. The three figures on each curve give the ratio of the metal oxides in the sequence K_2O - CaO - SrO . Inversion occurs at $Y = 2$.

of the structure but is solely the sum of atomic properties (this also applies, for example, to the density and the refractive index, which likewise show no inversion).

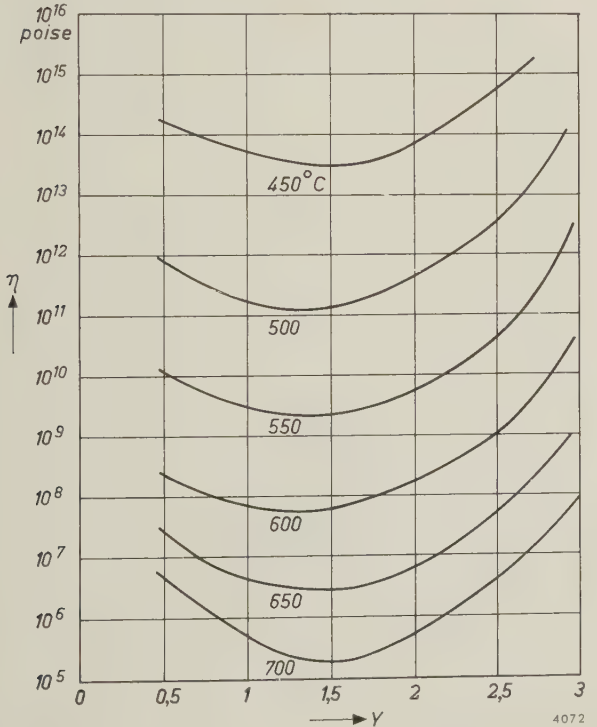


Fig. 8. Viscosity of $\text{Na}_2\text{-K}_2\text{O-MgO-CdO-ZnO}$ silicate glasses, at various temperatures, as a function of Y (equimolar quantities of the various metal oxides). Owing to the presence of intermediates (Mg^{++} , Cd^{++} , and Zn^{++} ions) the calculated value Y_c , plotted here, is not the same as the actual value Y_r (which is unknown) and will be smaller. Hence the fact that the slopes of curves reverse their sign at a lower value than $Y = 2$.

To conclude this section it may be remarked that the development of invert glasses constitutes in a certain sense a refutation of the classical theories concerning the structure of glass. The view formerly held was that a random three-dimensional network was essential to the vitreous state. We have seen, however, that such a network need not be present at all, *provided the metal ions show a sufficient variation in size and charge*. It appears, then, that the condition for realizing a vitreous state must be

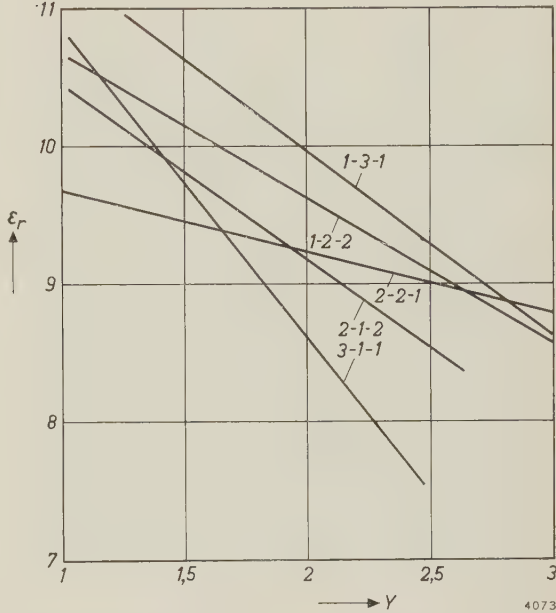


Fig. 9. Relative dielectric constant ϵ_r of K_2O - CaO - SrO silicate glasses as a function of Y , measured at 1.5 Mc/s. The mole fractions of the metal oxides are indicated in the same way as in fig. 7. No inversion occurs. This is due to the fact that the dielectric constant is not governed by the coherence of the structure, but solely by atomic properties.

formulated somewhat more widely: whereas in conventional glasses it is the disorder of the network that promotes the vitreous state, in the invert glasses the vitreous properties are due to the disorder of the metal ions.

Glass built up from microscopic domains of different structure and composition

In recent years experimental indications have been forthcoming to show that glass, which appears homogeneous to the eye, is in reality built-up from microscopic domains, differing one from the other and varying in size from 0.01 to 0.1 μ . How these domains come about is not known with certainty. It is thought that they are formed in the liquid state, when certain phases are separated. In certain

glasses these domains can be observed with an electron microscope; in others heat treatment is necessary to separate the phases more distinctly (see fig. 10a, b).

It is probable — at least in many cases — that these domains differ in their chemical composition, but whatever view is held of their nature, their existence means at all events that the original concept of a completely random network extended throughout the entire mass of the glass cannot possibly be correct. In so far as such a network exists it can only extend over short distances⁸⁾.



Fig. 10. Electron micrographs of sodium borate glass which is optically perfectly clear. a) glass that has received no after-treatment, b) glass heat-treated for $2\frac{1}{2}$ hours at 500 °C. (Taken from: W. Skatulla, W. Vogel and H. Wessel, *Silikattechnik* 9, 51, 1958.)

⁸⁾ A rough calculation shows that a spherical domain of 0.1 μ diameter and of average vitreous composition contains only 10^6 to 10^7 tetrahedra.

In this connection reference may also be made to refinements of the theory proposed by Russian investigators⁹⁾. In their view too, the structure does not show the degree of randomness suggested by Zachariasen's theory. Special grounds for this conclusion were provided by attempts to interpret the results of experiments with infrared absorption and small-angle X-ray scattering. They showed that it is necessary to assume the existence of domains with a more ordered structure side by side with domains having a "vitreous" structure. These "microcrystalline" domains, which are supposed to have the character of strongly deformed crystal lattices, are referred to as "crystallites". They are thought to merge one into the other *via* domains of gradually decreasing order. Variations in chemical composition might correspond to these transitions. The situation described is represented schematically in fig. 11a, b, after Porai-Koshits⁹⁾.

As a commentary on fig. 11b we give as our opinion that the various domains will not have such divergent compositions as is suggested. It is very unlikely that a glass will contain domains side by side, the one built up of tetrahedra with four bridging oxygen ions (SiO_2) and the other of tetrahedra with two bridging oxygen ions and two non-bridging oxygen ions ($\text{Na}_2\text{O} \cdot \text{SiO}_2$). If this were so, one could certainly not expect discontinuous changes in particular properties (examples of which have been given in the previous section) to occur at very specific values of Y corresponding to a simple physical model. On the other hand it is true that Y represents an average value, the material being after all a glass. In a glass with $Y = 3$, for example, there will not only be tetrahedra with three bridging oxygen ions, but also tetrahedra with four or two bridging ions. For $Y > 3$ there will undoubtedly be some tetrahedra with two bridging oxygen ions, and, conversely, for $Y < 3$ there will be some tetrahedra with four bridging oxygen ions. Their number, however, will be relatively small. It may be said then the glass will be found to contain domains of different character, as sketched in the above figures and manifested for example, in the phase-separation phenomena discussed. These domains, however, will differ only slightly in composition.

Network imperfections

After what has been said it will be clear that various concepts concerned with the crystalline state are evidently also applicable to the vitreous state.

⁹⁾ E. A. Porai-Koshits, *Glastechn. Ber.* 32, 450, 1959.

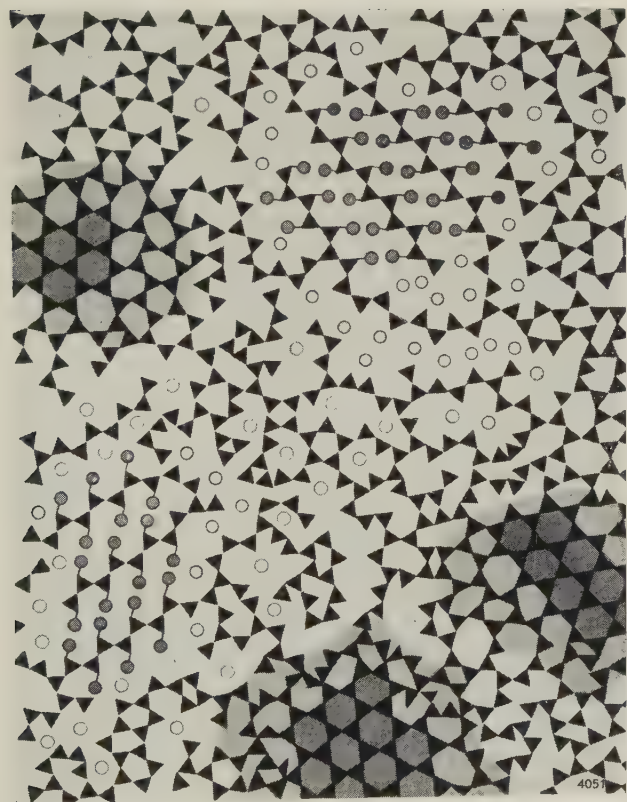


Fig. 11. Two-dimensional representation of the structure of *a*) vitreous SiO_2 , *b*) glass of composition $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$. (After E. A. Porai-Koshits, *Glastechn. Ber.* **32**, 450, 1959.) The crystalline domains (crystallites) are clearly recognizable. The degree of crystalline ordering is indicated by light and dark shading. In the view of the present writer, the interstices in (*a*) are in reality not so irregular as represented here. Oberlies and Dietzel have shown by X-ray diffraction measurements that the network of vitreous SiO_2 is largely built-up of six-ring conglomerates of tetrahedra¹⁰). In (*b*) we see domains of crystalline SiO_2 which, via vitreous SiO_2 and a vitreous region which also contains Na^+ ions, gradually merge into two regions whose structure closely resembles that of crystalline $\text{Na}_2\text{O} \cdot \text{SiO}_2$ (regions with dark circles).

In the last twenty years, it has been realized that all crystalline substances show lattice imperfections. Apart from two-dimensional imperfections, such as grain boundaries, there are also linear discontinuities (dislocations) and "point defects". We shall deal at greater length with the latter, in view of their particular importance in glass. In any given lattice, atoms may be missing here and there (*vacancies*). Atoms may be found at sites where, according to the arrangement of the lattice, they should not properly be situated (*interstitial atoms*). Lattice sites may be occupied by atoms alien to the lattice (*foreign atoms*). Finally, these three types of imperfection may occur with a positive or negative charge (*F centres*, *V centres*, etc.).

The above concepts have become a commonplace to investigators of the crystalline state, and have made it possible to gain a better insight into the mechanism of numerous physical phenomena. In the case of solids of simple structure, such as halides and chalcogenides, quantitative descriptions of such phenomena have in fact been given with the aid of these imperfections¹¹).

In spite of the complicated and irregular nature of vitreous systems, fruitful use has been made of several of these concepts in connection with the vitreous state.

Point defects in the vitreous network

As stated, point defects in particular are of importance in the vitreous network¹²). Although more or less the same classification has been maintained as for crystals, the absence of regularity in the network has made it necessary to introduce a modified convention with somewhat less sharp definitions.

Fig. 12, top left, represents a part of the Si-O network of quartz glass. The following three kinds of modifications may be introduced in this network.

An oxygen ion may be missing; we then speak of a vacancy. An oxygen ion may be added, which is then called an interstitial ion. (Strictly speaking, the term interstitial is out of place in relation to glass; follow-

¹⁰) F. Oberlies and A. Dietzel, *Glastechn. Ber.* **30**, 37, 1957.

¹¹) See e.g. G. W. Rathenau, *Imperfections in matter*, Philips tech. Rev. **15**, 105-113, 1953/54; H. G. van Bueren, *Lattice imperfections and plastic deformation in metals I*, Philips tech. Rev. **15**, 246-257, 1953/54; Y. Haven, *Lattice imperfections in crystals, studied on alkali halides*, Philips tech. Rev. **20**, 69-79, 1958/59.

¹²) Linear discontinuities are hardly to be expected in glasses in view of their disordered structure. As regards superficial discontinuities, a glance at fig. 10 shows that these do exist in glass. Little is known about them as yet, but it is certain that their closer investigation will be of considerable importance to the further development of the technology and applications of glass.

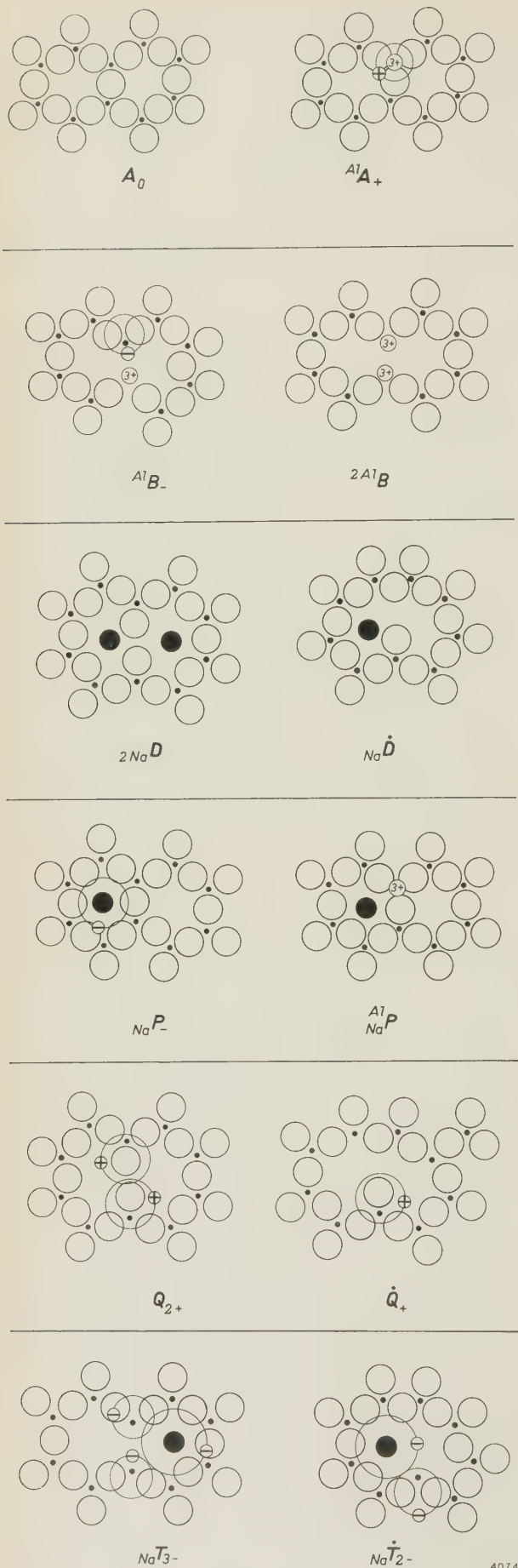


Fig. 12. Schematic representation of a “perfect” Si-O network and of various possible network imperfections. The symbol A_0 is assigned to the perfect network. All network imperfections given here are electrically neutral. This need not necessarily be so, of course, but it is usually the case. A_1A_+ is an imperfection in which an Si^{4+} ion is replaced by an Al^{3+} ion plus a captured hole. A_1B_- is an oxygen vacancy with a neighbouring aluminium ion substituted for a silicon ion, and a captured electron. (The captured electron and the charge gained due to the substitution of Al^{3+} for Si^{4+} compensate the charge lost through the absence of the oxygen ion.) $2A_1B$ is an oxygen vacancy occupied by two aluminium ions substituted for silicon ions. $2NaD$ are two paired non-bridging ions and two network-modifying sodium ions. NaD represents an unpaired non-bridging oxygen ion and a network-modifying sodium ion. NaP_- is a network-modifying sodium ion which has captured an electron. A_1NaP is a network-modifying sodium ion with a neighbouring aluminium ion substituted for silicon. Q_{2+} represents paired non-bridging oxygen ions with two captured “electron holes”. Q_+ is an unpaired non-bridging oxygen ion with a captured “electron hole”. NaT_{3-} is an oxygen vacancy, a network-modifying sodium ion plus three captured electrons. NaT_{2-} is an oxygen vacancy, a network-modifying sodium ion plus two captured electrons.

ing the old terminology, it is also the practice to say that a bridging oxygen ion is replaced two non-bridging oxygen ions.) Finally, a metal ion may be thought to occupy one of the large interstices that are always present in the Si-O network: this is referred to as a foreign ion (network modifier).

These three possibilities may also occur in combination, which, in principle, yields eight types of imperfection. The two combinations, however, where the bridging oxygen ion is replaced by a vacancy and at the same time by two non-bridging ions, cannot of course occur, so that only six remain. We shall call these, rather arbitrarily, A, B, D, P, Q and T; see Table II¹³⁾.

Table II. Possible imperfections in Si-O networks.

Symbol	A	B	D	P	Q	T
Oxygen vacancy	—	×	—	—	—	×
Non-bridging (interstitial) oxygen ion	—	—	×	—	×	—
Network-modifying ion	—	—	×	×	—	×

(As regards the three imperfections specified in the table, “A” thus represents a perfect network; but the reader is referred to the text and to fig. 12.)

¹³⁾ A. Kats and J. M. Stevels, Philips Res. Repts. **11**, 115, 1956.

The imperfections designated by these group symbols are more closely specified by superscripts and suffices to the letters. Typical examples of network imperfections are shown in fig. 12, illustrating this closer specification of possible imperfections. The place top left of the symbol is reserved for a superscript which indicates the ion replacing the silicon ion (e.g. $^{Al}A_+$ and ^{2Al}B). The subscript in front of the symbol denotes the nature of the network modifier (e.g. $_{2Na}D$ and $^{Al}_{Na}P$). A superscript behind the symbol denotes the replacement of oxygen by another ion (e.g. substitution by F, not indicated in fig. 12). The subscript behind the symbol denotes the number of captured electrons or "electron holes" (e.g. $^{Al}A_+$, ^{Al}B , $_{Na}P_-$, Q_{2+} and $_{Na}T_{3-}$).

Some network imperfections in fig. 12 require further explanation. In the case of vitreous silica in which a small amount of Na_2O is built in, the imperfections will be of the type $_{2Na}D$. Similarly, paired non-bridging oxygen ions will also be found in silicate glasses having a relatively low metal-oxide content. However, in glass networks with a relatively high concentration of metal oxides, which are much more loosely built, the non-bridging oxygen ions will be found *unpaired*. These cases are denoted by a point above the symbol. It need hardly be said that, in addition to \dot{D} centres (e.g. $_{Na}\dot{D}$), the corresponding \dot{Q} centres (e.g. \dot{Q}_+) and \dot{T} centres (e.g. $_{Na}\dot{T}_{2-}$) may also occur.

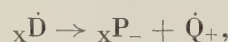
Network imperfections and physical phenomena in glasses

We shall now briefly outline the grounds on which the presence of certain centres may be inferred, after which we shall consider various examples of phenomena which are closely related to the existence of these centres.

Some idea concerning the centres likely to be encountered may be given by the results of a chemical analysis. In many cases, however, this is not enough, for the analysis provides no information on the manner in which the components or impurities occur, and the quantities involved in practice are often too minute to be detected by chemical analysis.

Various physical methods of measurement have therefore been used, and with their aid — and the suitable combination of results — it has proved possible to detect quite a number of centres. Measurements of optical absorption and of paramagnetic resonance have been of particular value in investigations of the vitreous state ¹⁴⁾.

Silicate glasses can often be described as an Si-O network containing \dot{D} and/or \dot{D} centres. As a rule, these cannot be demonstrated by the physical methods mentioned. The situation is quite different, however, if the glass is exposed to ultraviolet, X- or gamma radiation. In glasses containing numerous \dot{D} centres, these are the points where the radiation takes hold, as it were: an electron is released from the oxygen ion, the associated metal ion usually moves a certain distance and again captures an electron, so that ultimately a reaction takes place which can be described as follows:



where X denotes, say, an alkali atom.

The resultant $_XP_-$ centres show optical absorption at a wavelength that depends on the nature of the alkali ion. For example, the $_{Li}P_-$ centre exhibits absorption at 4200 Å, the $_{Na}P_-$ centre at 4600 Å, and the $_{K}P_-$ centre at 4750 Å. In the cases considered, absorption has also been observed at about 3000 Å which is independent of the nature of the alkali ion and must be attributed to the \dot{Q}_+ centre.

A similar picture has been obtained from paramagnetic resonance measurements. These are capable of demonstrating two kinds of centres, one of which must contain an unpaired electron and the other an unpaired electron-hole. The so-called g-factors thereby found for the first kind of centre were shown to be dependent on the nature of the alkali ion (1.960, 1.964, 1.966, 1.976 and 1.974 for $_{Li}P_-$, $_{Na}P_-$, $_{K}P_-$, $_{Rb}P_-$ and $_{Cs}P_-$, respectively). The g-factor of the centre with the electron hole, on the other hand, was found to be independent of the alkali ion (2.011) ¹⁵⁾.

For completeness it should be noted that, apart from releasing an electron, irradiation may also, through a secondary reaction, cause the release of an oxygen ion, which gives rise to a B centre. Where a P centre has been formed near this site, T centres may occur, detectable by absorption peaks in the region of 6200 Å.

Effects as here described are responsible for the discolouration of glass sometimes observed during and after irradiation. A case in point is the discolouration of the glass in X-ray tubes after a certain period of operation. Since the reactions that produce the centres responsible for such discolouration

¹⁴⁾ On paramagnetic resonance, see e.g. J. S. van Wieringen, Philips tech. Rev. **19**, 301, 1957/58.

¹⁵⁾ J. S. van Wieringen and A. Kats, Philips Res. Repts. **12**, 432, 1957.

are reversible, moderate heating is sufficient to remove the effect. At room temperature and below, however, the colour centres can be preserved for a considerable time.

Discolouration of this kind can often be very troublesome, and therefore means have been sought to counteract it. One successful method of dealing with the difficulty is to introduce small quantities of cerium oxide. The electrons liberated by irradiation in such a glass are captured by complexes of cerium ions and P centres. As a result, the absorption of light takes place at a lower wavelength than in the original glass, namely at $<3500 \text{ \AA}$, where the absorption is no longer perceptible to the eye.

Examples of such "controlled compositions", which lend special properties to glass and thus make special applications possible, have become too numerous to mention since the introduction of the concept of network imperfections. Glasses can be "composed", for instance, which discolour strongly when exposed to certain radiation. Glasses of this kind can be used for measuring extremely small doses of X-rays or gamma rays, the discolouration produced in the glass being a measure of the intensity of the radiation investigated.

Special importance also attaches to glasses which are capable of almost completely absorbing short-wave radiation without discolouring. Such material is suitable, for example, for observation-windows exposed to nuclear radiation.

Another effect studied is the presence of OH groups in glass, as a result of traces of water originating from the raw materials or from the flames in the melting furnace. Scholze has investigated the network imperfections involved (in our terminology $\text{H}\bar{\text{D}}$) by infrared absorption measurements¹⁶).

The OH groups in glass can occur in two different states. They may be "free", or they may be associated with a non-bridging oxygen ion and thus form a hydrogen bridge. Scholze showed that the absorption bands in the infra-red spectrum at $2.75\text{--}2.95 \mu$ must be attributable to the first kind of OH group and that at $3.35\text{--}3.85 \mu$ to the second kind¹⁷). The knowledge of this relationship affords a better understanding of various effects encountered in glass, as the following examples illustrate.

In the neighbourhood of a non-bridging oxygen ion there is always a metal ion to be found (to compensate the charge). The greater the electrical field

of the ions the stronger will this metal ion be bound to the oxygen. It thereby enters into competition with the OH groups that form the hydrogen bridge. As the field-strength of the metal ion decreases (e.g. $\text{Li}^+ \rightarrow \text{Na}^+ \rightarrow \text{K}^+$) more OH groups of the second kind may thus be expected, the alkali-ion content remaining constant. It has in fact been found that the absorption at $3.35\text{--}3.85 \mu$ does indeed increase under these conditions.

Another example. The aluminium ion, like the silicon ion, is a network former. When SiO_2 mixed with Al_2O_3 is used as a glass-forming oxide, a network is produced which is poorer in oxygen than if only SiO_2 had been used, there being fewer non-bridging oxygen ions (smaller X). If the molar fraction of Al_2O_3 is made equal to that of the alkali oxide it is even possible to produce a network *without* non-bridging ions. This is observable for example, from the complete absence of infra-red absorption of the second kind of OH groups (which are bound to non-bridging oxygen).

Finally, when the temperature is raised it may be inferred from the change in the infra-red absorption that the first kind of OH group increase in number at the expense of the second kind; this, again, is fully in accordance with the general picture outlined.

The knowledge of these phenomena has been turned to use in various ways. It is owing to the presence of OH groups that glass transmits infra-red radiation well only at wavelengths shorter than 2.8μ . For certain purposes it is desirable to widen the spectral range to be transmitted, for example where prisms are to be made for spectrometers that can also be used for the infrared part of the spectrum. Quartz glass is employed in such cases, and in order to obtain transmission to as far as possible in the infra-red efforts are made to expel all hydrogen from the glass. This can be done by heating the quartz glass for some time at 1000°C in a CO atmosphere.

Another method of increasing the infrared transmission is to substitute deuterium for the hydrogen. This substitution is accompanied by a shift of the infrared absorption edge, which then occurs at wavelengths of roughly 3.7μ instead of 2.8μ .

From the foregoing it will be clear that, by making use of the many and various imperfections that can occur in the vitreous network, it is possible to give glass widely diverse properties. The ability to control these imperfections, in conjunction with other modern developments discussed earlier, enables the manufacturer to produce a versatile range

¹⁶) H. Scholze, *Glastechn. Ber.* **32**, 81, 142, 278, 314, 381, 421, 1959.

¹⁷) The significance of a band at 4.25μ is not yet quite clear. Cf. R. V. Adams and R. W. Douglas, *J. Soc. Glass Technol.* **43**, 147, 1959.

of glasses to meet the multifarious requirements of science and technology.

Summary. In recent years a better insight has been gained into the structure of glass, through improvements and refinements of Zachariassen's theory. The relation between Y (average number of bridging oxygen ions per polyhedron) and various physical properties helps to explain the "boron anomaly" and other peculiarities in the behaviour of the physical properties

of glass with changing composition. If Y is smaller than 2, i.e. if the network is no longer coherent, the system tends towards crystallization. This tendency is counteracted by incorporating metal ions of differing size and charge. This has led to an entirely new category of glasses, called invert glasses. A new development is the discovery that glass is built-up from small domains of varying composition and structure (domains in which various phases have segregated and "crystallites"). The theory of the so-called network imperfections provides an explanation of the discolouring of glass under short-wave irradiation, and of various other vitreous properties. Some practical applications of this theory are discussed.

AUTOMATIC CONTROL IN GLASS MANUFACTURE

by P. M. CUPIDO *).

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As in so many mass-producing industries, automatic control techniques have made their entry into the glass factory. In this article, after a brief survey of the manufacturing processes, we shall deal with the parameters that can be subjected to automatic control, and discuss the requirements to be met by the instrumentation.

The following considerations are primarily concerned with glass manufacture as it is known at Philips, where glass is produced in the form of bulbs, tubes and rods. In many respects, however, they also apply to the mass production of glass in other forms.

Principles of glass manufacture

In glass manufacture a mixture of the raw materials (the batch) is heated in such a way that the temperature varies with time according to a specified programme. This time-temperature programme may be either discontinuous or continuous in nature.

An example of a *discontinuous* method is the melting of glass in pots. This is the oldest method of glass melting, and is still in use for glasses of special quality or for making relatively small quantities. The empty pots are placed in a furnace, which may be designed for only one pot at a time or for as many as 20. After the pot has been raised to a high temperature, the batch mixture is introduced. This consists of powdered oxides and carbonates together with waste glass (cullet). Because of the amount of air entrapped in the mixture, the thermal conductivity is low. It therefore takes a considerable time to heat. As the temperature rises, the melting reaction sets in, and this is accompanied by the generation of

gases which partly disappear into the furnace atmosphere and are partly trapped as gas bubbles in the foaming, viscous mass. The higher the temperature is raised, the lower becomes the viscosity, enabling the gas bubbles to rise more readily to the surface and escape.

The displacement of the gas bubbles sets up a movement in the glass which effectively promotes the desired chemical reactions. When the latter have ceased, no further gas bubbles are generated. The gases still entrapped now gradually escape, and the glass becomes more homogeneous in composition. This part of the process is known as "fining". The glass is then allowed to cool until it has reached the viscosity required for further working.

The mechanical production of large quantities of glass imposes demands on the manufacturing process that cannot be met by pot melting. A process better adapted to the purpose is that whereby the melting is done in a *tank furnace*. Here the charge and the molten glass are in direct contact with the walls and floor of the furnace. The floor, together with the part of the walls, forms the melting tank (or "end"). It is an oblong trough built up from blocks of refractory material. The batch is fed in at one end (the "dog-house") and the molten glass withdrawn at the other. At the melting end the charge is subjected to the necessary time-temperature programme, which consists of creating an appropriate temperature gradient along the trough and carefully controlling the rate at which the glass traverses that gradient. As opposed to pot melting, this is a *continuous* process.

It would be ideal if all the glass issuing from the melting tank had been subjected to exactly identical conditions. This is not the case, however. Owing to

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the complex currents that arise, and because of unavoidable "blind spots", the duration of flow through the melting tank differs for the glass in different regions of the tank. Good glass can only be obtained if no part of the mass is heated for too short a time, i.e. the duration of flow must be above a certain minimum. A long duration of flow is equally undesirable, however, for economic reasons and also for reasons of quality: if the glass stays for a lengthy period in the melting tank the composition of the molten mass changes, due to the disparate evaporation of certain constituents and to the solution of wall material. The duration of flow, then, must lie within critical limits.

An unchanging flow pattern in the melting tank is therefore of particular importance, and the conditions governing that pattern must be kept carefully constant. These conditions are: the method of feeding-in the batch mixture, the withdrawal of the molten glass, and, above all, the heat transfer in the melting tank and the temperature at various places above and below the glass surface.

To give some idea of how these and other conditions can be controlled in a continuous process, we shall examine a tank furnace in somewhat more detail.

A regenerative tank furnace

The heart of the furnace is the melting tank. This is built, without mortar, from flush-fitting blocks of refractory material. In the case we shall consider, the furnace walls contain a number of ports as inlets for the flames from oil burners. The distribution of the fuel over several burners allows accurate adjustment of the axial temperature gradient in the furnace. The oxygen required for combustion is drawn from the air entering the furnace through the burner ports. For reasons of fuel economy, the air is preheated in a heat exchanger, which derives its heat from the combustion gases passing to the chimney stack.

There are two preheating systems — recuperative and regenerative. The *recuperative* system is generally used only for relatively small furnaces, with a capacity of no more than twenty or thirty tons a day. In this system the air to be heated and the combustion gases flow through separate channels (the recuperator) divided by ceramic or metal partitions through which heat is continuously transferred.

For larger furnaces the *regenerative* system is more economical. The furnace is flanked on both sides by a box-like brick structure (fig. 1) with a refractory

lining and containing an open-stacked structure of fire-bricks ("checkers"). This structure (the regenerator) has a high heat capacity and offers little resistance to the alternating flow of the hot combustion gases and the air for preheating. As explained in the caption to fig. 1, the burners at each side of the furnace are operated alternately. The air needed is preheated in the one regenerator, whilst the combustion gases, on their way to the chimney stack, flow through the other regenerator, which thereby accumulates heat. After, say, half an hour the burner flames are extinguished, the gas flows are

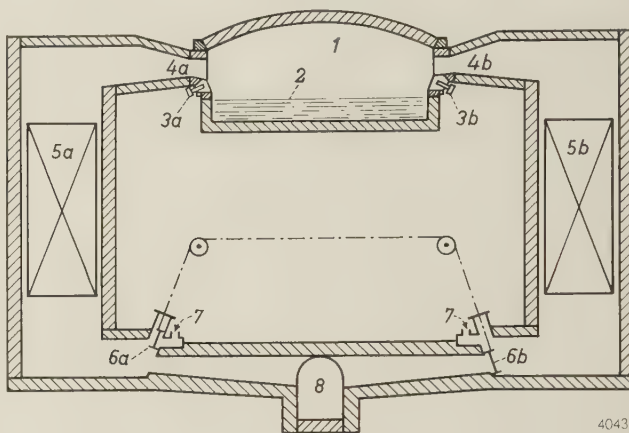


Fig. 1. Cross-section of a regenerative tank furnace. 1 furnace. 2 glass level. 3a, 3b oil burners. 4a, 4b burner ports. 5a, 5b regenerators. 6a, 6b reversal dampers. 7 combustion-air feed. 8 chimney flue.

With the dampers 6a and 6b as drawn, the burners 3b are in operation, the combustion air being preheated in regenerator 5b and the combustion gases delivering heat to regenerator 5a; burners 3a are extinguished. The situation is reversed every 20 to 30 minutes.

reversed, and fuel is fed to the burners at the other side, and so on.

In the recuperative system the burners work continuously, there is no reversal and a temperature equilibrium is established in the heat exchanger; as a result, constant processing conditions are easy to achieve. By contrast, in the regenerative system the temperature of the heated air is continually changing, and each reversal severely disturbs the conditions prevailing in the furnace. In spite of this drawback — which can be reduced by shortening the reversal periods — the regenerative system is preferred for quantity production because, as we have said, it is more economical. The reason is the better heat transfer in the regenerative heat exchanger, in which the air is preheated to a temperature of 1000 or 1100 °C, i.e. 300 to 400 °C higher than in a recuperator.

Further processing

After leaving the melting tank the glass enters the working tank (or "end"), likewise a refractory structure but of smaller dimensions. (The terms "melting end" and "working end" date from the time when glass manufacture was not yet an automatic process; raw materials were always added at one end of the tank and the glass-blower worked at the other.) In automatic production — with which we are primarily concerned — the main function of the working tank is for letting the glass settle to a lower temperature. The glass flowing out of the melting tank has a temperature of 1400 or 1500 °C, which must be reduced to 1000 or 1100 °C for working. Part of this reduction, which must be uniform and thus calls for suitable time and space, is effected in the working tank.

From the working tank the glass flows into one or more *feeders*. These are long channels of refractory material, in which a proper combination of cooling and heating gives the glass a constant and uniform temperature. The feeders terminate at the glass-working machines. Depending on the product to be made, the glass is fed to the machine continuously or discontinuously. A machine that turns out glass tubing or rods receives a continuous supply, whereas a bulb-blowing machine (see the relevant article in this number) is fed with successive portions termed "gobs" which are cut off with special shears (fig. 2; see also figs. 3 and 4 on pp. 321 and 322).

Parameters amenable to automatic control

Having outlined the production process in a regenerative tank furnace we shall now consider how the processing conditions can be controlled ¹⁾.

Automatic control of furnace temperature

We have already mentioned the great importance of a constant heat transfer from the furnace atmosphere to the glass. To this end it is a first prerequisite to keep the temperature in the furnace and its distribution carefully constant. In the case of an oil burner the temperature is easy to control by placing a suitable sensing element, e.g. a thermocouple, near the flame and transmitting the signal to a valve-operated control device which regulates the rate of supply of oil. The operation of such a simple control system will now be examined, and will be shown to fall short of requirements.



Fig. 2. The stream of glass flowing through the feeder to the glass-working machines is cut into "gobs" by automatic shears. The photograph shows a gob on the point of dropping into a machine for pressing the screens of television picture tubes.

The fuel is atomized by air or steam under pressure. As the pressure rises, the droplets get smaller and mingle more rapidly with the air feed, thus accelerating the combustion and making the flame shorter. The flame transfers its heat to the ambient in two ways: by *radiation*, mainly from the luminous cone, and by *convection* via the combustion gases. A shorter flame thus means that less heat is given up by radiation. Since the same amount of energy per second is still being supplied to the burner, the result is that the combustion gases get hotter. If the thermocouple is located at a position where the heat transfer is mainly governed by convection, the consequence of increased atomizing pressure is that the control system reduces the oil flow, which is of course not the action required. The controller should return the atomizing pressure to the correct value. The simple control system described would therefore be unsatisfactory.

A rise in oil temperature would have a similar effect. The fuel used is a heavy oil whose viscosity only permits satisfactory atomization at a temperature between about 80 and 90 °C. Its viscosity is so temperature-dependent that a variation of a few °C is sufficient to cause a marked change in the atomization. A higher oil temperature thus results in a finer oil mist, a shorter flame and, in the case described, a higher thermocouple temperature, again reducing the oil feed.

Improvement can be sought by mounting the thermocouple at a place where it is least directly influenced by the flame, for instance in the crown of the furnace. The disturbances mentioned will then be less noticeable. A disadvantage, however, is that

¹⁾ See also P. M. Cupido, Some views on automatic control in glass factories, *Glastechn. Ber.*, 5th Internat. Congress on Glass, Sonderband 32 K, Heft I, pp. I/1-I/5, 1959.

the thermocouple is now more or less part of the crown, whose heat capacity is very high. Changes in flame temperature will thus be measured with a considerable lag, making rapid and stable automatic control impossible.

The right answer to this problem is to provide every condition governing the properties of the flame with its own control circuit. The first thing to do is to insert a *thermostat* in the oil line to keep the fuel temperature constant, and a *pressure regulator* in the atomizing system.

The next step is to keep the *oil flow rate* constant. For this purpose a constriction is included in the line (orifice plate or venturi), and the pressure drop across it acts, via a regulator, on a control valve in the oil line. This system quickly corrects disturbances without any risk of instability. A fall in oil pressure — due, for example, to partial clogging of a filter — can be corrected in a matter of a few seconds.

Also of importance are the *flow rate of combustion-air* and its *temperature*. Let us consider the flow rate first. This directly determines whether the flame is surrounded by an oxidizing or a reducing atmosphere, and also influences the length and radiation of the flame. It is therefore desirable to measure and regulate the flow of the combustion air. The construction of most furnaces does not allow this, however. The resistance which the burner ports and the regenerator offer to the air flow causes the air to be distributed over the ports in a way that can hardly be controlled. Attempts to control the air distribution by means of dampers in the burner ports have been made, but have all come up against severe practical difficulties.

A system that is both feasible and highly effective relies on a separate regenerator for each burner port. The air required by each burner is fed-in at the bottom of the appertaining regenerator. The air feed can be controlled by a system similar to that used for the oil feed, that is to say the air flow is measured with an orifice plate or venturi tube and kept constant by means of a regulator and control valve. The oil and air regulators are coupled via a *ratio controller*, which maintains the desired ratio of oil to air when one or the other is being varied.

The temperature of the combustion air remains an intractable problem. This temperature is highest immediately after the burners have been reversed, and then gradually falls. The temperature drop can be reduced by shortening the period between successive reversals. The period must not be too short, however, since every reversal — as mentioned above — severely disturbs the prevailing conditions: all flames are extinguished during that operation and

the composition of the furnace atmosphere alters radically. The most favourable compromise is usually to fix the period between 20 and 30 minutes. To minimize the disturbance, the reversal itself must be made to take place as rapidly as possible.

Automatic reversal

The reversal of the system is obviously an operation that should be done automatically, the more so since a furnace with separated regenerators in any case involves various operations which must be carried out in rapid succession. We shall now see what these are and the sequence in which they are required to take place.

Suppose that the burners on the left are in operation. When the moment for reversal arrives the first operation is to shut off the oil feed to the left-hand side, and the second to lower the pressure of the atomizing air.

It is not permissible to shut off the supply of atomizing air completely, air being required for cooling the idle burners in order to prevent residual oil carbonizing and causing a blockage. It is equally impermissible to leave the full atomizing pressure on the burners, in view of the quantity of cold air that would then enter the furnace (about 5% of the total combustion air). Hence the *reduced* atomizing pressure on the burners when not in operation.

The next operation is to supply combustion air via the regenerator chamber on the right, its first function being to dispel the combustion gases still present in the chamber. Not until this has been properly done may the atomizing air for the right-hand burners be raised to the requisite pressure and the oil feed turned on. If the latter were done too soon, lack of oxygen would prevent immediate combustion of the atomized oil, resulting in a badly smoking flame and possibly after-burning in the regenerator.

To make these simple operations take place automatically it is necessary to introduce a number of reliable safety measures. Defects in the reversing mechanism, for example, must never give rise to a situation where oil continues to flow to the burners but no combustion or atomizing air. The consequence could obviously be a serious explosion.

Fig. 3 shows a safeguarded reversing system which has been developed for the automatic furnaces in the Philips glass factories. The initial reversing command is given by a clockwork control timer, and each successive command cannot be issued until the preceding one has been properly executed. Reversal is effected in a time of 10 to 15 seconds. The system is so designed as to shut off the oil feed automatic-

ally in the event of a fault or failure, e.g. of the mains voltage or the compressed air. The operation of the system is described in the caption to fig. 3.

Automatic control of the gas pressure in the furnace

A parameter not yet mentioned, but whose constancy has an important bearing on the process, is the *pressure inside the furnace*. The combustion

process gives rise in the furnace to a certain pressure distribution and the gases present acquire certain velocities. By measuring and controlling the pressure at a suitable point it is possible to stabilize the distribution pattern as a whole. The pressure in the furnace must be somewhat higher than outside, otherwise cold air would be sucked in through various apertures and adversely affect the tempe-

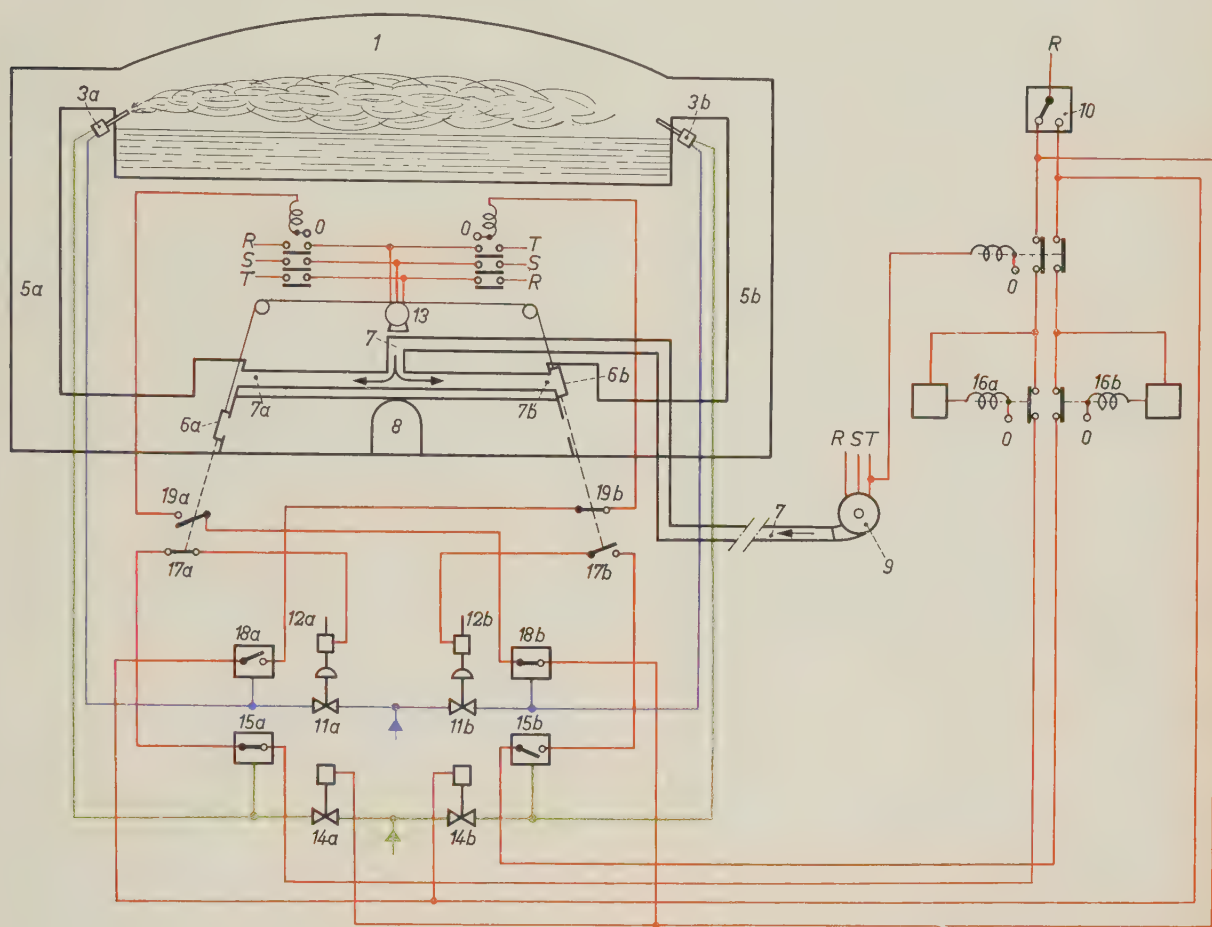


Fig. 3. Simplified layout of automatic reversal system in use in Philips glass factories. 1 tank furnace with burners 3a and 3b, regenerators 5a and 5b, reversal dampers 6a and 6b, duct 7 for the supply of combustion air from blower 9, and chimney flue 8. The clockwork control timer 10 delivers at preset intervals the signal initiating the reversal.

Blue: oil lines. Green: atomizing-air lines. Red: electric wiring. RST0 three-phase mains.

In the situation as drawn, burners 3a are working. Oil is fed to them via valve 11a, atomizing air via valve 14a, and combustion air via channel 7a and the hot regenerator 5a. The combustion gases are removed via the cooled regenerator 5b and the chimney flue 8. The oil valve 11a is held open against the action of a strong spring by a pneumatic motor, which receives air only so long as the electromagnetic cut-out 12a is energized.

The reversal is initiated by the switching arm in timer 10 changing its position. The cut-out 12a ceases to be energized, oil valve 11a closes, and the flames on the left are extinguished. Switch 18a, which was off, changes to the on position as the oil pressure drops, and switches on the electric motor 13. The latter now effects the reversal: damper 6a rises (connecting regenerator 5a to the chimney and closing the air feed 7a), and damper 6b descends. On reaching their new positions, the

dampers switch off the motor 13 by actuating switch 19b.

By altering the position of control valve 14a the initial signal from timer 10 causes the atomizing air on the left to drop to the required low pressure. As a result the pressure-sensitive switch 15a moves to the off position. This switch, in series with contacts 17a, is incorporated in the line for energizing cut-out 12a; the oil feed to the burners 3a cannot therefore be restored until the pressure of the atomizing air has been raised and the dampers are in their correct positions.

To supply oil to burners 3b, valve 11b must be opened. This involves energizing cut-out 12b, which is not possible until switches 15b and 17b are on. Switch 17b comes on when damper 6b descends. For 15b to close, the atomizing pressure of burners 3b must be sufficiently high, i.e. valve 14b must be wide open. The timer 10 further ensures that 14b is opened wide, not immediately, however, but only after a delay determined by relay 16b. This delay is necessary to allow the combustion air to dispel the combustion gases from regenerator 5b. This latter operation is promoted by a special "flushing" signal which fully opens the control valve for the combustion air and the valve in the chimney flue, thus enabling the oil feed to be switched on earlier. In the event of a failure in the electric supply or the compressed-air supply, the oil feed is automatically shut off.

rature distribution, and perhaps also the combustion. The difference in pressure should only be slight, however, since the escape of hot gases entails a loss of heat and moreover accelerates furnace wear.

In manually-regulated tank furnaces the positive pressure is adjusted with stack dampers, which are generally broad and heavy cast-steel plates in the flue to the chimney stack. The control range is covered by moving the damper up or down a few centimetres. For automatic control such a damper is scarcely suitable: its large mass (often increased by counter-weights) does not lend itself to rapid control, and the available maximum displacement of only a few centimetres precludes the precision and stability required. It would be an improvement to mount a narrower and much lighter damper on the existing damper; the reduced width then gives a greater stroke and the smaller mass allows faster and more accurate control.

An effective and inexpensive method of automatic control depends on the use of an adjustable "artificial draught" (*fig. 4*). In the chimney flue 1, in front of the damper 3, a round aperture is made which is fitted with a short side-pipe 5. This contains a butterfly valve 6, which can be moved by a pneumatic or electric servo-motor 7 much faster than is possible with the stack damper in the systems just discussed. The butterfly valve controls the pressure prevailing in front of the damper by admitting a greater or smaller quantity of air.

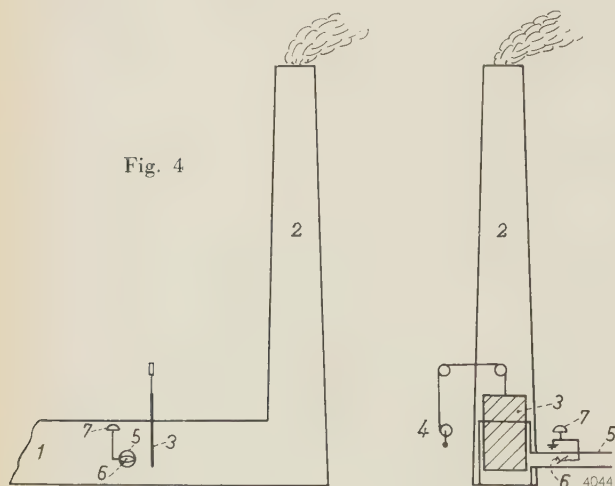


Fig. 4

Fig. 4. Automatic control of the pressure inside the furnace by an artificial draught. 1 flue through which the combustion gases from the furnace enter the chimney stack 2. 3 damper, adjustable with hand winch 4. 5 side-pipe with butterfly valve 6, rotated by servomotor 7.

Fig. 5. A short chimney using air injection avoids the difficulties caused by gusts of wind with high chimney stacks. 1 flue for exhausting the combustion gases. 2 air-injector with blower 3, control valve 4 and servomotor 5. 6 adjustable damper producing the correct under-pressure upstream of the damper. 7 short chimney.

Even with this system, however, the control action is not fast enough to deal with the consequences of gusts of wind at the mouth of the chimney. Gusts of wind give rise to often steep-fronted pressure waves which travel at the speed of sound into the furnace itself, where they upset the prevailing conditions. In this respect a high brick stack is inferior to a short, possibly metal chimney in which an appreciable negative pressure can be created with the aid of an air-injector (*fig. 5*), thereby minimizing the effect of pressure variations caused by strong gusts. The correct pressure in the furnace is obtained by suitably adjusting the flow resistance in the flue by means of a damper.

The system using a short chimney, however, is not without its drawbacks. The short chimney does not conform to the regulation in many countries that large quantities of combustion gases containing a high percentage of sulphur (as in the case of fuel oil) may only be discharged into the atmosphere above a certain height. Furthermore the energy required for the injection pushes up the running costs to a multiple of those incurred with a high stack.

Some of Philips glass factories use high chimneys, others low. *Fig. 6* shows an outside view of the pressed-glass works at Eindhoven, with its two high chimney stacks.

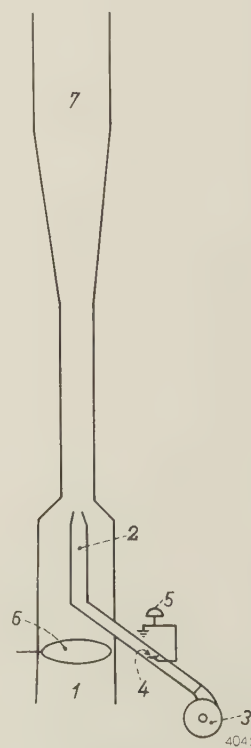


Fig. 5

Automatic control of glass temperature and level in the feeders

We now come to the feeders, which represent the last stage of the molten glass on its way to the machines where it is worked. The feeders are required to deliver per unit time a *constant quantity* of glass of *constant viscosity*. Since there is no practical means of directly measuring and regulating the viscosity, an indirect means of controlling it is adopted, that is by controlling the *temperature* of the glass. However, the

viscosity is not solely dependent on the temperature but also on the composition of the glass. Changes in composition sometimes occur in the form of irregularly distributed inhomogeneities (cords), which may be due to non-uniformities

Performance criteria required of control systems

A principal requirement to be met by control equipment is that, if the value of the controlled quantity changes, the correct value should be rapidly restored. A limit is set to the speed of the

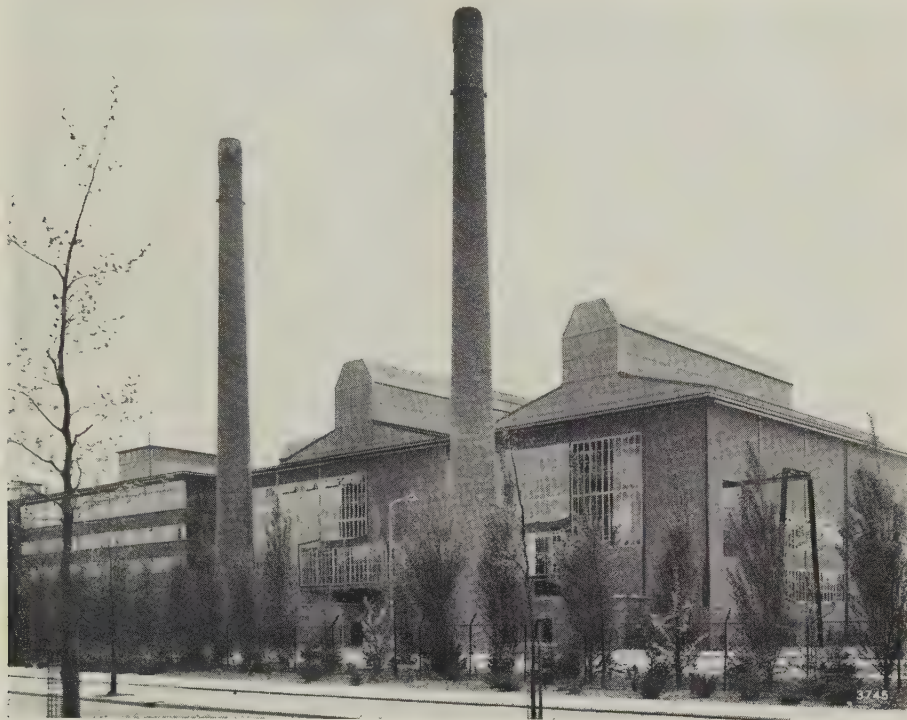


Fig. 6. Philips pressed-glass factory at Eindhoven.

in the batch composition. The less such deviations occur, the better is the temperature control system able to maintain the desired viscosity.

The *quantity* of glass which the feeder delivers per unit time depends on the viscosity and level at the effluent end. It is therefore necessary to keep the level of the glass constant. This level is therefore continuously measured, and deviations from the desired height are fed-back to act on the rate at which the batch mixture enters the furnace. Controlling the automatic batch feed in this way also helps to keep the melting conditions constant, as well as the flow pattern in the tank furnace.

Experience has shown that accurate level control prolongs the life of the melting tank appreciably.

The molten glass attacks the walls of the tank, especially at the level of the glass surface. This ultimately causes a groove to appear, which is narrower the less the level of the glass varies. That this is attended by a longer tank life is presumably to be explained by the fact that, in the narrow groove, the glass is virtually stationary, so that after some time it becomes saturated with material dissolved from the wall, and further corrosion proceeds much more slowly.

control action by the properties of the controlled process and of the control instruments used. If this speed is exceeded the system becomes unstable, that is to say, after a disturbance the value of the controlled quantity continues to oscillate at a certain amplitude around the desired value. This phenomenon has been discussed in this journal in an article concerned with process control systems in general²⁾. We shall briefly recapitulate the salient points.

The operation of a control system is based on comparing the measured value of the controlled quantity with the desired value. Two main categories may be distinguished: discontinuous and continuous control. The first category, for example simple two-step or on-off control, has the advantage of considerable simplicity and reliability. A process controlled by a discontinuous controller, however, is by nature unstable: the controlled value oscillates continually around the desired value. In cases where the amplitude of the oscillation is excessive continuous control is indicated. The controller may have

²⁾ H. J. Roosdorp, On the regulation of industrial processes, Philips tech. Rev. 12, 221-227, 1950/51.

proportional or integral action, whereby the position of the final control element is proportional to the deviation ε from the desired value, or to $\int \varepsilon dt$ respectively. Purely proportional action has the disadvantage that the desired value is never entirely reached, which is not the case with integral action. The best result is obtained as a rule by combining proportional and integral action. A derivative action, proportional to $d\varepsilon/dt$, may be added. It has a damping function and is only employed to improve the stability of control systems where particularly fast corrective action is required.

reduce the lag in a part of the process and in the measuring unit.

We have seen that, to control the level of glass, it is necessary to measure the level continuously, deviations from the desired height being made to act on the rate at which the batch mixture is fed in. Between the melting tank and the working tank — i.e. in front of the point where the level is measured — there is a communicating passage, the “throat”, which serves for skimming-off impurities and inhomogeneities on the surface of the glass and for preventing undesired currents along the bottom of the melting tank. For the latter reason the throat

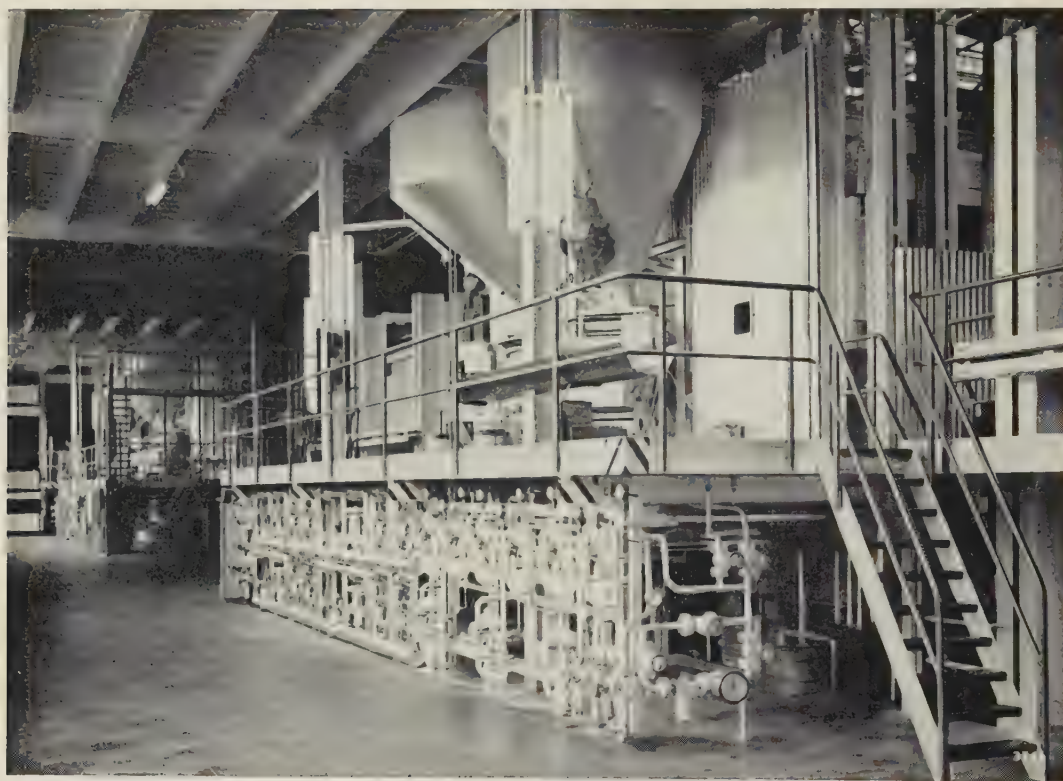


Fig. 7. The two furnaces in the pressed-glass factory in Eindhoven. Above the gallery can be seen the raw-material hoppers that open onto the feed machines. The corrugated plates shield off radiation from the furnace. Under the gallery are some of the valves and control elements of the control system.

Sufficient stability is almost invariably to be ensured by not raising the sensitivity of the control equipment too far. There are cases, however, where the response of the system would be too slow, because of the transfer lag or dead time of the process itself, of the measuring unit or of the final control element. Reduction of the lag of a final control element was discussed above in connection with controlling the pressure in the furnace (where a heavy damper was replaced by a lighter one). We shall discuss two other practical examples to illustrate how it was possible in certain cases to

must not be too wide. In some existing plants, however, it was so narrow that a disturbance of the level in the melting tank reached the detecting element only after a considerable delay. This delay was reduced by widening the throat.

Our last example relates to the equipment for measuring the temperature at the top of the furnace. Following the old and familiar practice, a block was placed in the crown of the furnace with a hole drilled into it for the thermocouple. The block protected the thermocouple and also acted as a radiation shield, and had a wall thickness of a few centimetres.

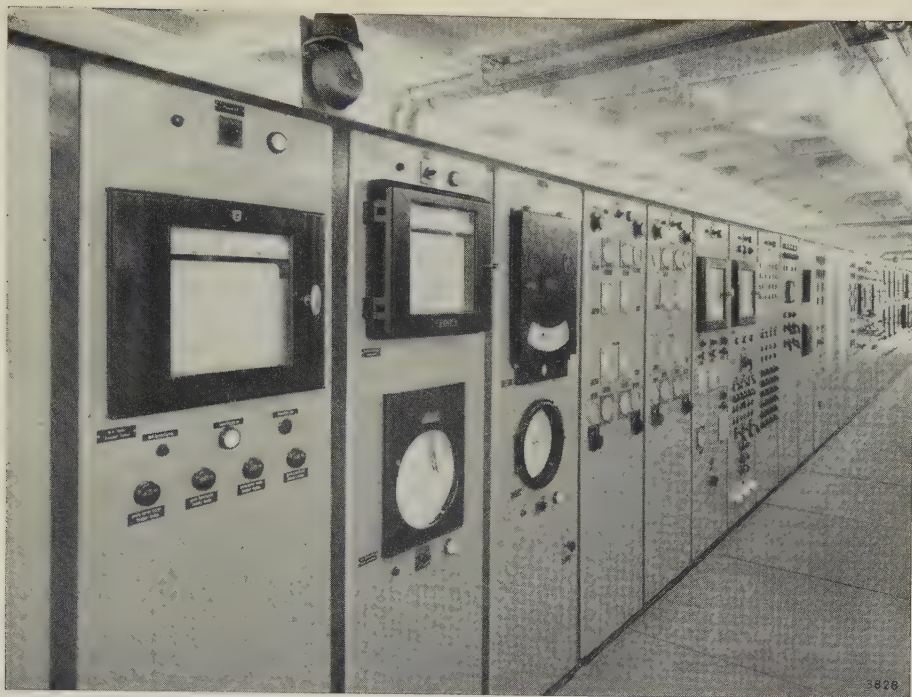


Fig. 8. Instrument racks of the (largely pneumatic) control system for the plant shown in fig. 7. Recording and other instruments, pilot lamps and control buttons can be seen.

The result was that the measured temperature was appreciably lower than that of the furnace, and that the response to changes in the furnace temperature was subject to a considerable dead time. The temperature difference and the response lag were substantially reduced by placing the thermocouple in a thin-walled refractory sheath passing through the crown block and projecting about 10 cm into the furnace. A marked improvement was thus obtained in the automatic temperature control.

A property which all automatic control equipment must possess, especially for continuous processes, is a high degree of *reliability*. This is a matter of both plant design and choice of control equipment. In the plant it is necessary to ensure that any component which is at all vulnerable is readily accessible and can be quickly replaced. This also applies to control valves, orifice plates, etc., incorporated in the pipelines. It should be possible to isolate all these components from the rest of the equipment, and they should be provided with individual bypass lines that can be shut off, the latter to allow replacement without having to close down the plant. To facilitate fault-finding, readily accessible and well-planned points should be provided where the necessary check measurements can be made. It is desirable that defects should be automatically localized and signalled by pilot lamps. In the choice of control

equipment, too, reliability is the dominant factor, the cost being a secondary consideration.

Fig. 7 shows a view of the furnaces in the pressed-glass factory at Eindhoven. Under the platform can be seen the valves of the largely pneumatic control system. The associated control panels, with meters, pilot lamps, etc., are to be seen in fig. 8.

Hitherto, the control devices used in glass manufacture have been almost exclusively pneumatic. Recently, however, the use of electronic controllers has started to gain ground. The fact that these devices possess the high degree of reliability required for industrial processes is partly attributable to the transistor. Electronic systems are particularly suitable wherever fast automatic control is called for.

Summary. A discussion of the parameters amenable to automatic control in glass production is introduced by a short description of the glass-manufacturing process. Recuperative and regenerative tank furnaces are touched upon. Stabilization of the process by individual automatic control of all quantities influencing the process, is shown to be desirable. These quantities are: the temperature of the fuel oil, the oil flow rate, the pressure of the atomizing air, the combustion air flow rate, the oil to air ratio, the pressure inside the furnace, and the temperature and level of the molten glass in the feeders to the glassworking machines. A discussion is devoted to the automatic reversal of the burners in a regenerative furnace, which must take place every 20 to 30 minutes. In the choice and installation of control equipment — hitherto largely pneumatic — emphasis is placed on reliability. The use of electronic control equipment in glass production is gradually gaining ground.

MECHANICAL PRODUCTION OF BULBS FOR ELECTRIC LAMPS AND RADIO VALVES

by P. van ZONNEVELD *).

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It is now many years since hollow glass objects, such as bottles, jars and similar containers, have been manufactured mechanically, largely replacing manual methods. Manual as opposed to mechanical production is preferred only where small quantities are involved and possibly also where it is desired to make a variety of products at the same time or to change quickly from one type of glass to another.

Machines for producing lamp or valve bulbs must be capable of turning out a fairly thin-walled product without marked variations in thickness and possessing — for lamps, at least — reasonable optical properties. Bulbs cannot therefore be made on a bottle machine.

The machines that fabricate articles direct from *molten glass* fall into two main categories, namely those which pick up the glass by suction from the surface of a glass tank, and those which receive their supply from an orifice in the bottom of the reservoir containing the molten glass. The latter may again be sub-divided into machines that receive their charge in portions or “gobs”, and machines to which glass is fed continuously.

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As we shall see, it is not economical to make very small objects with these machines. For this purpose special machines have been developed whose starting material is not molten glass but *glass tubing*.

In this article we shall discuss both main types of machine. Three machines designed for the working of molten glass will be dealt with. Particular attention will be devoted to a machine developed at Eindhoven which has the merit of working without loss of glass: the gobs fed to the machine need be no heavier than the bulbs to be fabricated.

As regards machines that work from glass tubing, we shall deal first with an 18-head machine designed, again at Eindhoven, for working short sections of tubing, one per bulb. This will be followed by a brief discussion of the way in which new machines have been and are being evolved on the same principle.

Before proceeding to mechanical glass-working, it will be useful to recall the method of blowing glass by hand. The glass-blower starts by dipping and rotating the end of his blowpipe into the molten glass and thus making a “gather” (*fig. 1a*), care being taken to gather no more and no less than is roughly required for the product. He then rolls the mass of

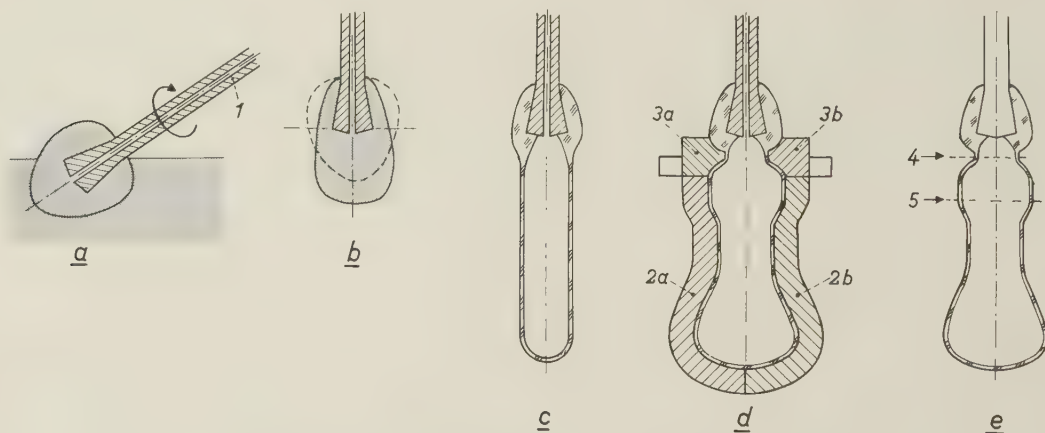


Fig. 1. The principal phases in off-hand glass-blowing.

a) “Gathering” the glass: the end of the blowpipe 1 is dipped into the molten glass (shaded) and rotated to pick up a lump of glass of the required size.

b) The gather is rolled on a plate to reduce the amount of glass that cannot be blown (above the horizontal dashed line).

c) The hollow mass of glass — the “parison” — to be enclosed in a blow-mould. The glass-blower swings, inverts and otherwise manipulates the parison to distribute the glass in such a way that the blown product will not show excessive variations in wall thickness.

d) The blown bulb inside the two halves of the mould (2a and 2b), which mate against the halves of the cap (3a and 3b). As can be seen, the blowpipe remains outside the mould.

e) After blowing the bulb is severed from the blowpipe (at 4) and the excess glass is cut off from the bulb (at 5). The glass still adhering to the blowpipe is removed before the glass-blower makes a fresh gather.

hot glass on a plate to reduce the portion which, adhering around the pipe, cannot be blown (fig. 1b). This being done, he blows for a moment into the mouthpiece and then closes it with his thumb. Thermal expansion of the air causes the hollow mass thus formed — called the “parison” — to swell out. By swinging the parison to and fro the glass-blower helps it to reach the required elongation faster than it would under the force of gravity alone. While the air is expanding he may also hold it up vertically or obliquely for a moment, to ensure the required distribution of the glass. Next, he encloses the parison between the two halves of a split mould (“open and shut” mould), and blows until the glass fits against the sides (fig. 1c and 1d). During this process the glass cools down to rigidity. Finally, it is severed from the blowpipe, and the blower is able to make a fresh gather. His product is not, however, complete at this stage. As a rule, excess glass has to be sheared away from the top (fig. 1e). In fig. 2 a number of glass-blowers can be seen at work. Some of the steps in the production process described will be encountered in the machines used for working molten glass, which we shall now discuss.

Machines for making bulbs from molten glass

The Eindhoven 16-head machine

The gobs of molten glass worked by the 16-head machine developed at Eindhoven are automatically cut at regular intervals from the viscid stream of glass issuing in a constant delivery from an orifice in the furnace floor. The cutting shears (see figs. 3 and 4) are two knives with roughly V-shaped cutting edges, which slide one over the other.

The machine itself consists of a continuously rotating turntable on which are mounted 16 gob-



Fig. 2. Glass-blowers at work. The man on the right has just made a “gather” and has started to form the parison. The man in the centre (foreground) has completed the parison and is about to close the blow-mould (with a pedal). The third is inspecting a product fresh from the mould. The workman on the left removes the bulbs from the blowpipes. Between the first two glass-blowers (foreground) is a table for the rolling operation.

receiving stations and 16 complete glass-blowing units; the former are operated mechanically, the latter for the most part pneumatically. Each glass-blowing unit has its own set of control valves, which ensure that the unit turns out one bulb on every

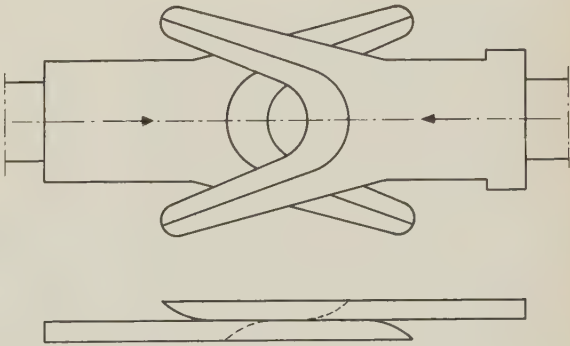


Fig. 3. Shears for cutting the viscid stream of glass issuing from underneath the furnace into “gobs” (schematic). The two V-shaped knives slide one over the other in the direction of the arrows.

revolution of the turntable. The machine thus produces 16 bulbs per revolution.

As soon as a gob is severed it drops into a small tray of a given receiving station. The tray, which at that moment is situated close to the periphery of the turntable, is then slid back under the blow-head of the corresponding glass-blowing unit. The manner in which this takes over the glass from the tray and turns it into a bulb will be described with reference to *fig. 5a*.

In this figure, *A* is the gob tray (blue). It is mounted in a holder (also shown in blue) which can move radially in a groove in the turntable *B*. When the

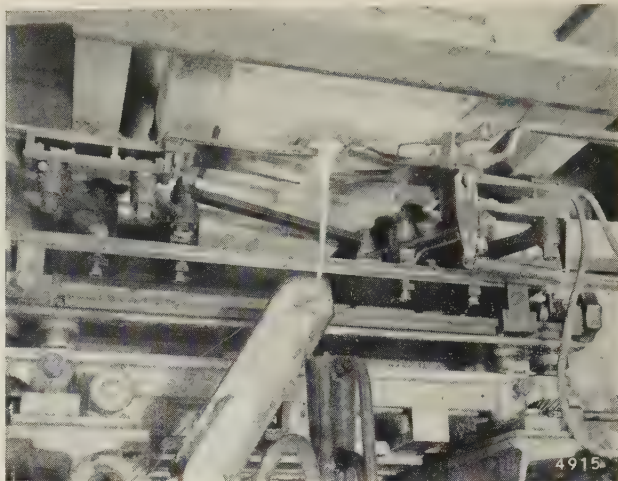


Fig. 4. Gob shears mounted under the furnace floor. Since the machine had to be stopped for taking the photograph, the glass stream is led off through a gutter at the side.

head rests on the edge of the tray, and the plunger slides downwards with respect to this part, thereby slightly compressing the spring *F* (yellow). The plunger and the remaining part of the blow-head

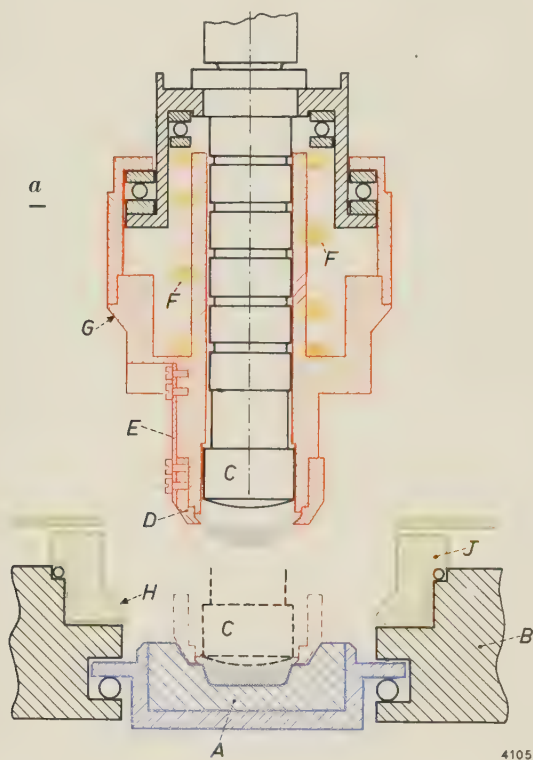
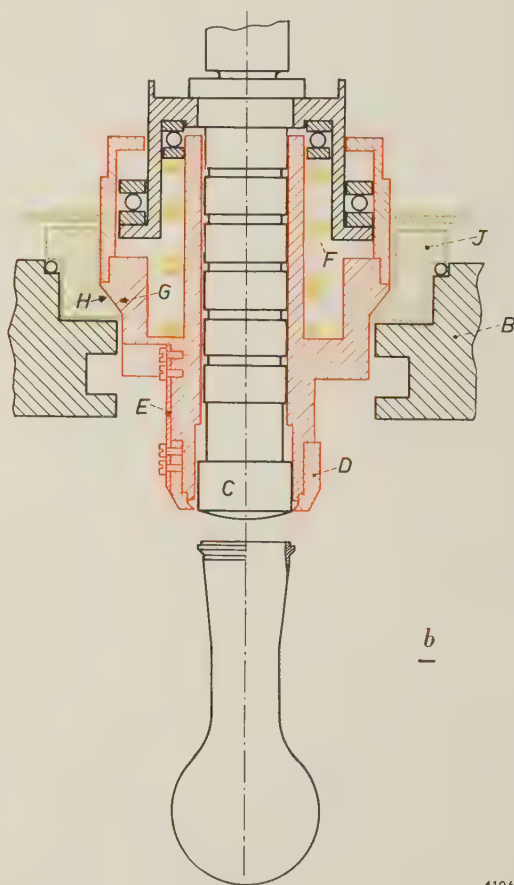


Fig. 5. *a*) Schematic cross-section of a blow-head (red-black-yellow), a gob receiver (blue) and part of the turntable. *A* is the gob tray, mounted on a slide which moves in a radial groove in the turntable *B*. *C* blank plunger. *D* one of the claws which hold the glass (shaded) forced into them by the plunger. (The blanking position is represented by dashed lines.) *E* leaf-spring to which *D* is attached. *F* spring (yellow). *G* tapered edge of red part which, during the elongation of the parison, the blowing of the bulb and the ejection from the head, rests on the tapered edge *H* of the permanently rotating ring *J* (green).

b) The blown bulb is ejected by the plunger *C*, the red part of the head still resting on the ring *J*. In this operation the spring *F* is compressed somewhat more than in the blanking operation.

tray is centred under the blow-head, the latter descends (see dashed lines) and the plunger *C* presses the glass (shaded) into the claws *D*. These are flexibly mounted to leaf-springs *E*, and close together at the sides so that the glass cannot flow out between them. In this blanking operation the red part of the blow-



then return to their initial position (this is the position represented in *fig. 5a*; the red part is now suspended from the part outlined in black) and the empty gob receiver returns to the edge of the turn-

table. The blow-head is now able to carry out the further operations. It again descends and abuts with its tapered edge *G* against the mating edge *H* of a ring *J* (green), which is in continuous rotation on the turntable. The red part of the blow-head is thus set in rotation too. Its lower portion, carrying the transferred gob or blank, projects under the turntable and is immediately above the open blow-mould. At this point the glass, which began to elongate the moment it was picked up, is reheated (in the case of certain shapes of bulb) by a burner mounted underneath the turntable.

To accelerate the elongation process and ensure that a bulb of roughly constant wall-thickness is produced, a few short puffs of air are blown into the parison. The air for this "puffing" operation is supplied through a duct inside the plunger stem, and enters the parison by flowing around the plunger when the latter is in the position shown in fig. 5*a*. It will be noted that, compared with the glass-blower, the machine is limited in its manipulations for properly distributing the glass in the parison; it is therefore particularly important for the puffs to be of the correct strength and duration. When the elongation is far enough advanced, the two halves of the split blow-mould close and air is blown into the parison, which thus acquires the contour of the mould. The mould then opens again and the bulb is released from the claws. This is done by the plunger, which again descends and presses on the mouth of the bulb, thereby forcing open the claws. (The part shown red cannot descend since it rests on the turntable, and spring *F* is fairly strongly compressed — fig. 5*b*.) The ejected bulb drops on to a conveyor belt. Finally, the blow-head returns to its starting position, and the gob receiver and blowing unit are ready to accept a fresh charge. The movement of the turntable is synchronized with that of the shears by driving them both with synchronous motors.

It should be added that so-called "paste" moulds are used, i.e. moulds lined with adherent carbon — in the present case a layer of graphite. While the mould is open the lining is sprayed with cold water. During the blowing operation, when the bulb continues to rotate inside the mould, a small quantity of water vapour forms which precludes actual contact of the glass with the mould, giving the product a very smooth surface.

The vertical movement of blow-head and plunger is brought about pneumatically by means of a vertical piston above the blow-head. In fig. 6, which shows the arrangement schematically, the positions are marked as assumed by the piston during the various stages of the fabrication process. It can be

seen that only the lowest (after ejection of the bulb) is governed by the dimensions of the cylinder; the blanking and blowing positions are determined by the blow-head resting respectively on the gob receiver and the rotating ring.

The valves in the lines that supply and release the compressed air are mechanically operated. They, and the valves for the gas and air feed to the burner,

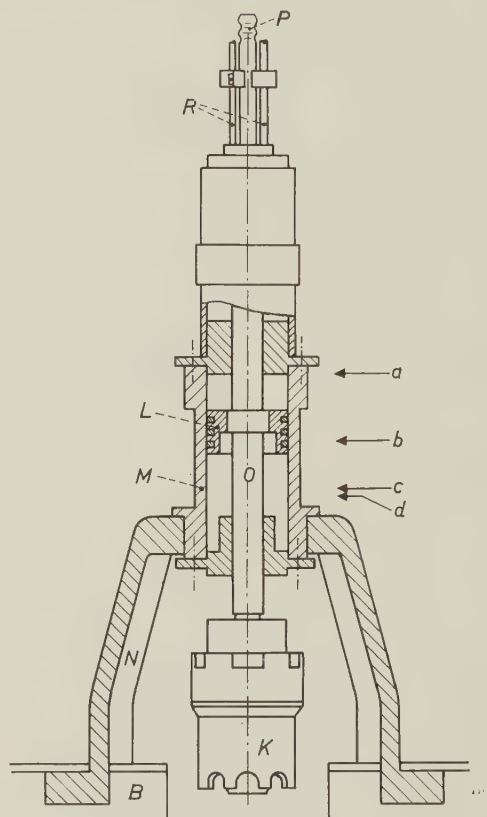


Fig. 6. The vertical movement of the blanking and blowing head *K* is effected pneumatically by means of a piston *L* travelling in a cylinder *M*. The cylinder is mounted by two supports *N* on the turntable *B*. The piston rod *O*, to the bottom of which the blow-head is mounted, also extends above the piston to provide for stops. The positions taken up by the piston in the various phases of the production process are: *a* position prior to blanking, allowing the slide with gob tray to move under the blow-head; *b* blanking position; *c* position for elongation and final blowing; *d* ejection position. The duct *P* is for the air feed; the tubes *R* conduct cooling water through the space between the inner and outer tube forming the piston rod.

are operated as follows. Mounted above each blowing unit, about 1 metre above the turntable, is an off-radial beam attached to the table and carrying the valves pertaining to the unit. The valves are operated by adjustable cams fitted underneath a fixed plate (fig. 7). As the machine rotates, the rocker arms of the valves pertaining to the sixteen blowing units all pass successively the same cams. Since it must be possible to vary the starting time

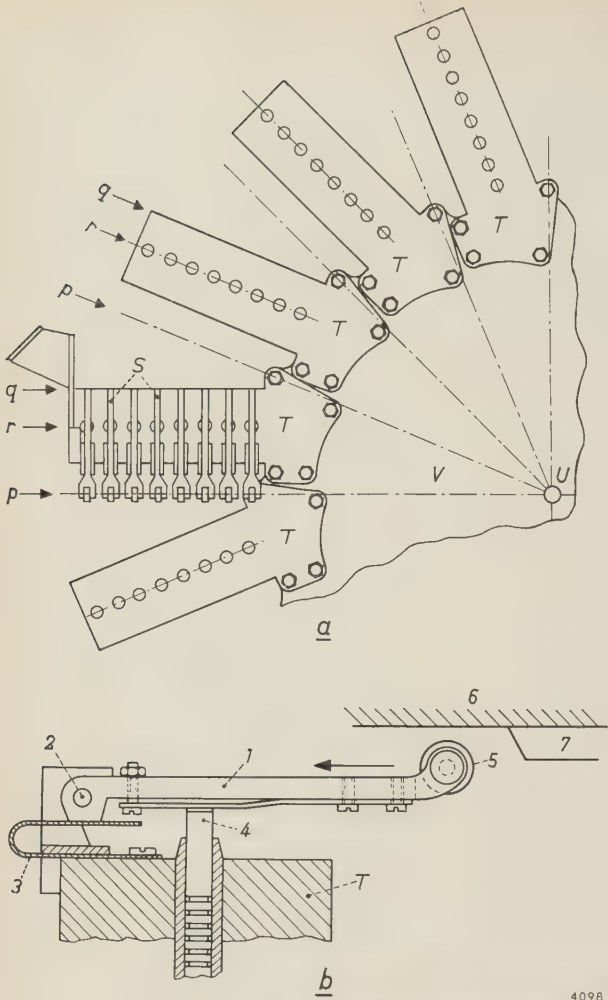


Fig. 7. a) The rocker arms S, which operate the valves, are mounted tangential to the turntable on the cross-beams T in such a way that the cam-rollers lie on the lines p intersecting the turntable axis (U). The rocker-arm pivots lie on the lines q, the valve plungers on the lines r. The 16 valve cross-beams are bolted to the central plate V, which is fixed to the turntable. The entire assembly thus rotates when the machine is in operation.

b) Side view of one of the rocker-arm assemblies. 1 rocker arm. 2 pivot, so designed that the lever can be removed by simply pressing-in the leaf-spring 3 and the valve plunger 4. 5 roller which travels along under the cam plate 6. 7 cam. The valve cross-beam moves in relation to the cam plate in the direction of the arrow.

In such machines the rate of production is governed by the longest operation at a given position, whereas in our case the speed at which the turntable revolves is the decisive factor, and this is governed solely by the total time needed to produce one bulb. The latter is about 15 seconds, and therefore the rate of production is just over one bulb per second, or roughly 4000 an hour. A continuously rotating machine is also mechanically to be preferred to one with intermittent action, particularly where large machines are involved. A third advantage is that machines equipped with complete blowing units can produce different kinds of bulbs at the same time. The only restriction is that the bulbs must all be of the same weight and must all be made with the cams in the same position.

Photographs showing a machine of the type described are to be seen in figs. 8 and 9. Fig. 10

and duration of every operation in order to establish the optimum conditions necessary for blowing good bulbs, each cam consists of two parallel adjacent plates which can be displaced with respect to each other in a direction tangential to the circular cam mounting plate.

A considerable advantage of this system, in which the machine keeps turning continuously, is that a bulb never has to "wait" for the beginning of the next operation, as it must do in machines not equipped with complete blowing units, where each operation has to be performed at a particular position whilst the machine is stationary.

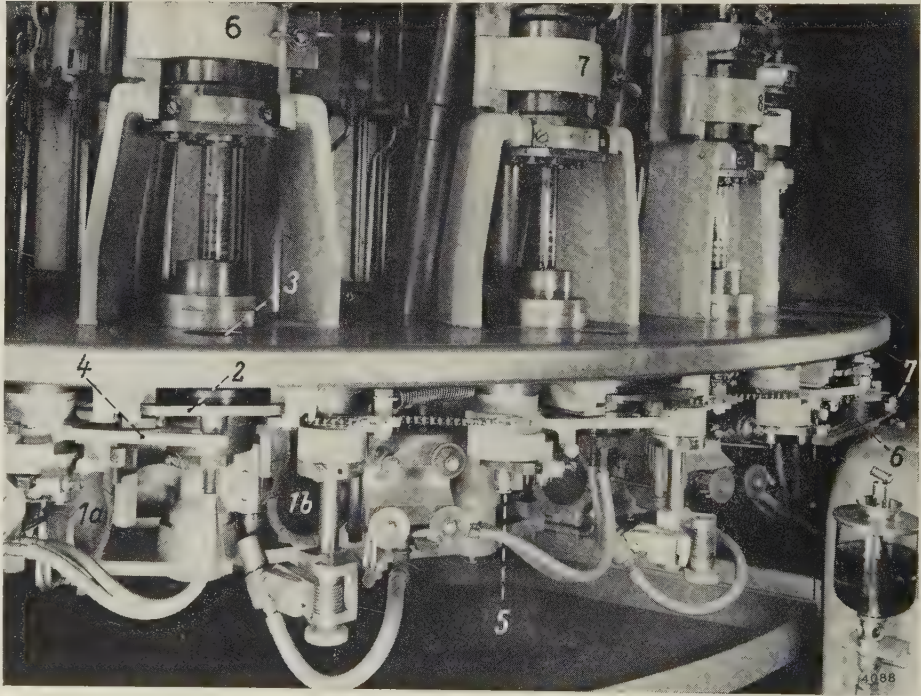


Fig. 8. Detail of the machine in fig. 9. Among the components that can be identified are the two mating halves of a blow-mould, 1a and 1b, and the slide 2. As soon as a gob has fallen through the hole 3 into the tray, the slide is pushed inwards by the lever 4, the forked end of which engages a roller. This lever is itself turned on a spindle by a cam 6 (extreme right of photograph) on the cross-beam 7. (The relevant spindle in one of the neighbouring blow units is indicated by the figure 5.)

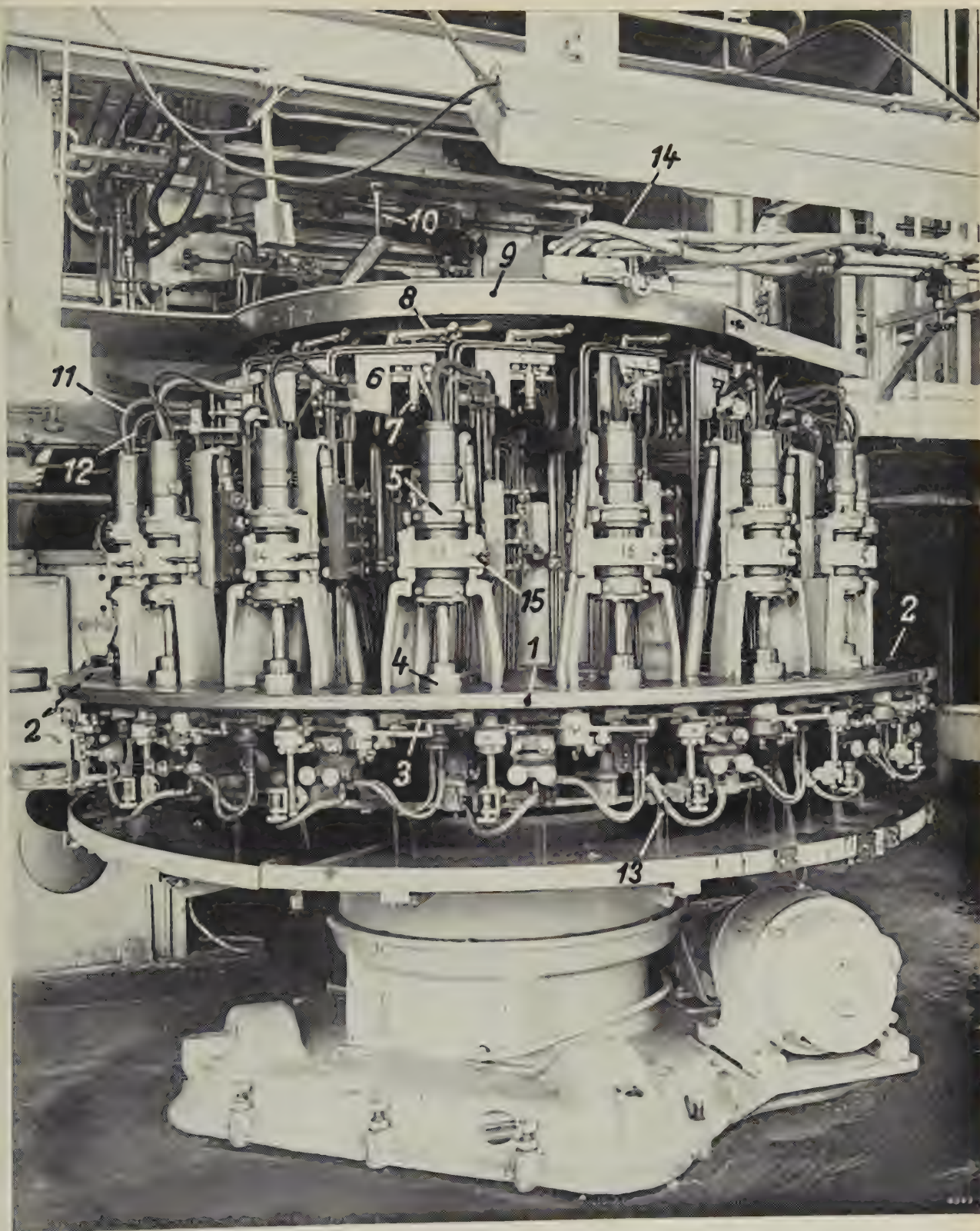


Fig. 9. Machine for making electric-lamp bulbs, equipped with 16 blowing units. 1 turntable on which the blowing units are mounted. 2 holes in the turntable through which the gobs fall into the receiving trays. These trays are mounted in slides 3. 4 blow-head in blowing position (in which case the blow-head projects under the turntable). 5 cylinder with plunger. 6 end of a cross-beam carrying control valves. 7 outer valve of the eight carried on one cross-beam. 8 rocker arm which operates this valve. 9 cam plate. 10 stream of molten glass flowing from

an orifice underneath the furnace (the glass was not fed to the machine when this photograph was taken). 11 air feed for puffing and blowing. 12 cooling-water line for piston rod. 13 burner for heating the elongating parison. 14 supply lines for gas, air (both for burners 13), oil and compressed air (for the blow-heads). After shutting-off the feed, disconnecting the hoses and unscrewing the fly-nut 15, a single manipulation is all that is needed to remove a blow-head together with its cylinder.

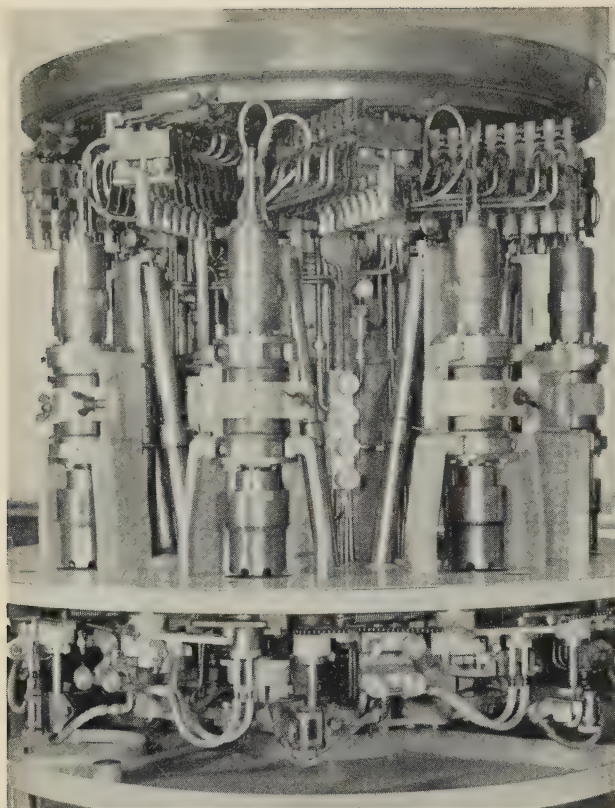


Fig. 10. Eight-head machine from which the 16-head type was developed. The construction here gives a better view of the valve-beams and the cam plate.

shows a similar 8-head machine in which various details are better visible. *Fig. 11* illustrates the layout of such a machine with respect to a glass furnace, and *fig. 12* the method of obtaining a constant delivery of glass gobs from the furnace. Since the machines work with no loss of glass, the furnace can be fairly small; a machine whose hourly output is 4000 bulbs of 32 grams each consumes in that time only 128 kg of glass. A small selection from the numerous kinds of bulbs that can be made on these machines is shown in *fig. 13*.

Although we speak of glass losses, no glass is in fact wasted. Any glass that may have to be cut away from a blown bulb to produce the shape required by the lamp factory is of course fed back to the furnace. The actual loss is in the heat needed for remelting, which amounts roughly to 75% of the heat necessary for making glass of the same temperature from the pure raw materials. In this connection it should be remembered, however, that in practice glass is never made from 100% raw materials but from a batch containing 30 to 50% of cullet (broken glass), added to obtain more readily a fluid mass possessing better thermal conductivity.

Finally, it should be mentioned that the machine is designed to allow numerous elements to be changed *during* operation. For instance, with a few manipulations an entire blow-head can be replaced, and the same applies to such components as the rockers

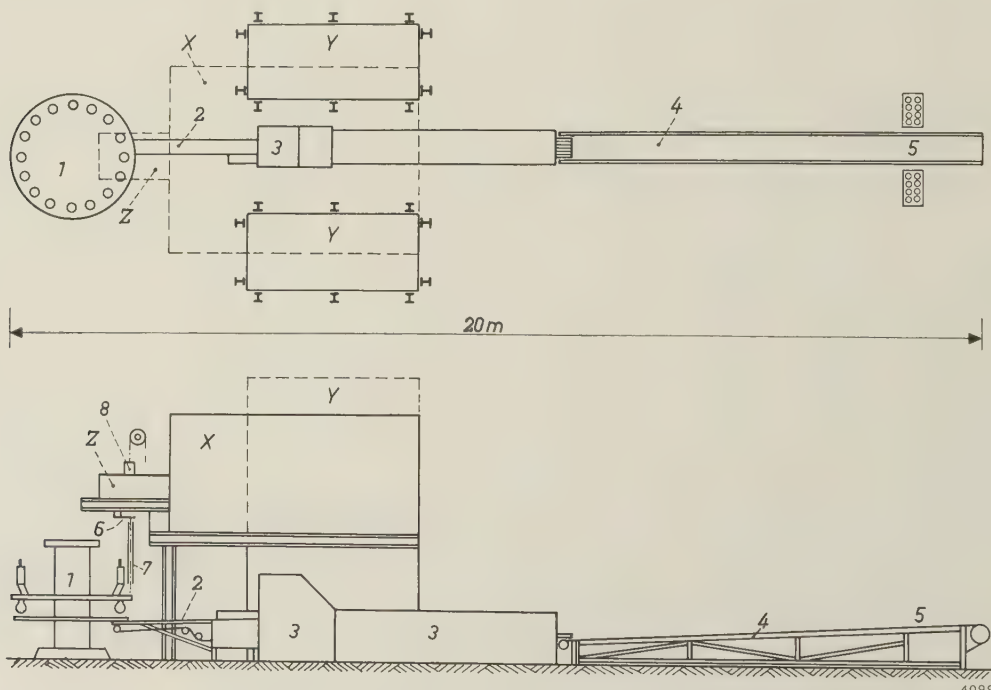


Fig. 11. Schematic layout of a manufacturing unit for the mechanical production of electric-lamp bulbs. a) Plan, b) side view. The whole plant is contained within a rectangle of $20 \times 5\frac{1}{2}$ metres. X glass furnace. Y furnace recuperators, in which the outflowing combustion gases heat the air flowing to the burners. Z part of glass furnace from which the bulb-blowing machine 1 is fed. The blown bulbs are carried by the conveyor 2 to the annealing oven (lehr) 3 (underneath the glass furnace), and by the conveyor belt 4 to the sorting room 5, where all bulbs are inspected. 6 shears for cutting gobs. 7 chute through which gobs drop into the receiving tray on the machine. 8 mechanism ensuring uniformity of the glass stream and constancy of delivery (see *fig. 12*).

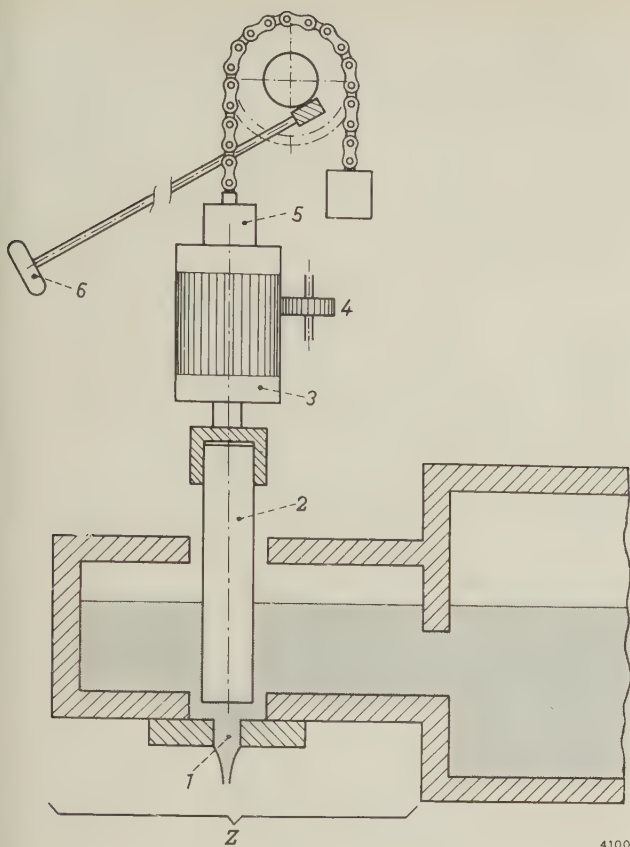


Fig. 12. Gobs of equal size and composition are obtained by introducing a rotating ceramic spindle 2 above the orifice 1 in the floor of the feeder Z of the glass furnace. The spindle is raised if the gobs are too small, and lowered if they are too large. The spindle, which is rigidly mounted to the bushing 3, is set in rotation by the pinion 4, whose teeth engage in those around the bushing. Height variation is made possible by the long teeth cut in the bushing. The whole assembly is mounted to a non-rotating bushing 5 suspended from a chain which passes over a sprocket wheel, operated via a worm transmission by the hand wheel 6.

on the valve cross-beams, the valves themselves, the slide carrying the gob trays, and the halves of the split blow-moulds. Where necessary the cams can also be adjusted whilst the machine is turning.

At the end of this section we shall return to the performance of the 16-head machine by way of comparison with the machines now about to be discussed.

The ribbon machine

Another machine which receives the glass from an orifice in the furnace floor is the so-called "ribbon machine", developed by the Corning Glass Works ¹⁾. The glass is not delivered in gobs, but flows from the furnace in a continuous stream and passes between two water-cooled rollers, which produce a ribbon from it. One of the two rollers is plain, the other has circular recesses or pockets. As a result the ribbon shows a series of regularly spaced protrusions, giving it rather the appearance of a strip of detonating caps for a child's pistol. Each of these protrusions comes exactly above a hole in a continuously moving metal conveyor belt, which carries along the ribbon on a horizontal plane, and the glass begins to sag down through each hole and assume a bulb shape. The ribbon now passes under a series of blow-heads, each of which is centred above the holes (the machine has scores of such heads, which are mounted on an endless belt and are thus able to travel along some way with the ribbon). As in the previous machine, air is puffed into the parisons to promote the elongation.

¹⁾ A description of this machine is given by F. V. Tooley, *Handbook of Glass Manufacture*, Ogden, New York 1953, pages 356 and 386.

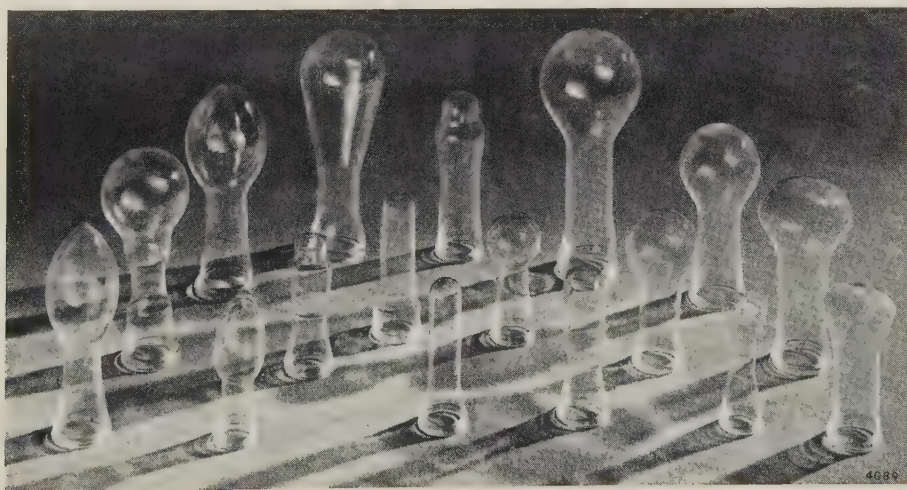


Fig. 13. Small selection from the many and various kinds of bulbs that can be made on the 16-head machine. Apart from the diameters, all bulbs have the same shape of rim, where they were held by the blanking and blowing heads.

Next, the parisons are enclosed in blow-moulds (a series of which are also mounted on an endless belt, this time under the ribbon) and the bulb is blown. After the moulds have opened again, the bulbs are allowed to cool somewhat and are finally broken off from the ribbon. Ribbon machines, then, always involve a certain loss of glass. Their production capacity, however, may be very high; the largest machines of this type produce some 60 000 bulbs an hour with a diameter of 60 mm (i.e. 1000 per minute or more than 1.4 million per 24 hours) or about 100 000 smaller bulbs (1600 per minute or 2.3 million per 24 hours).

The vacuum-and-blowing machine

The third kind of machines to be discussed in this section uses the so-called vacuum-and-blowing process, the portions of molten glass being gathered from the surface of the tank by suction. These machines are equipped with a swinging arm (or ram) which introduces the gathering cup into the furnace. As soon as the cup has gathered the correct volume of glass, it is swung outwards by the arm, automatically shearing off the tail of glass following it. The blank is then transferred to one of a series of blowpipes on a turntable, the blowpipe being at that moment vertical. Since these machines are also in continuous rotation, the arm must move around with the table when transferring the blank, which is of course a technical complication. After the transfer the arm turns back to its initial position, the blank cup is swung into the furnace again, and the process is repeated.

As soon as a glass gob is dropped on to a blowpipe, jaws at the end of the pipe close around it. These are so shaped and situated that, when the blowpipe is in the "blowing position", i.e. directed vertically downwards, the glass is held at the edge. As in the other machines discussed, a puffing operation now follows, and the parison is finally blown to shape in a split blow-mould mounted under each blow-head. This being done, the blow-mould opens and the bulb is then released by the jaws. The bulb now drops on to a conveyor belt and is carried to a burn-off machine where the thick glass edge held by the jaws (the moil) is removed. In these machines, too, a certain amount of glass is lost.

Bulb-making machines of the vacuum-and-blowing type exist in 6-head and 8-head versions, and may have one, two or four blowpipes per head²⁾;

²⁾ The single-arm machines are known as Westlake machines, those with two arms as Ohio and those with four arms as Ivanhoe machines. The Westlake machine is described in the book mentioned under reference¹⁾, and the Ivanhoe machine by W. S. Turner, *J. Soc. Glass Techn.* **13**, 393, 1929.

a 6-head machine with four blowpipes per head thus has altogether 24 blowpipes and delivers 24 bulbs per revolution. According to the number of blowpipes per head, there are one-, two- or fourfold ram arms.

The production capacity of these machines is roughly between 3000 and 6000 bulbs an hour, which is thus of the same order as that of the Philips 16-head machine.

Comparison of the various machines

To conclude this section on machines for working molten glass, we shall comment briefly on the possibilities and limitations of the various types of machine. We shall be particularly concerned with: 1) the production capacity, 2) the glass losses, 3) the versatility of the machines as regards diversity of products.

As regards production capacity, we have seen that the gob-fed machines are roughly equivalent. Their minimum time of revolution is determined by the time needed to make one bulb. The production of a machine can therefore only be stepped up by increasing the number of blow-heads. This is possible only to a limited extent, however, otherwise the machines would be unmanageably large. A limit is also set to the speed at which portions of glass are taken over from the furnace — a speed that increases in proportion to the number of blow-heads. Since the temperature and hence the viscosity of the glass are confined to specified limits, it would be necessary to make the orifice wider. The length of the severed gobs would then soon become too small in proportion to the thickness of the glass stream. A better solution is to use, say, two orifices and two pairs of shears, but this presents serious constructional difficulties. If a very high production capacity is required, the ribbon machine is therefore the appropriate type, its capacity, as we have seen, being a factor of 10 greater.

As regards glass losses, these have been shown to be zero in the Philips machine. In the other machines the usefully employed glass amounts on an average to roughly 50% of the total processed quantity, and very much less where small bulbs are made, e.g. of 15 grammes. It should be added, however, that bulbs as small as this cannot be produced entirely without loss of glass even on the Philips machine. These machines are not suitable for handling extremely small portions of glass, which cool down too quickly to be worked.

With regard to versatility, we have seen that the Philips machine can not only make bulbs of different types at the same time (given the same gob weight) but that the blow-mould can also be changed very quickly.

The considerable versatility of the Philips machine

described, and its low glass consumption, make it possible to equip a bulb factory with them which can economically turn out any kind of bulb in almost exactly the quantities required by a producer of electric lamps and radio valves. A glass factory thus equipped is able to modify its production programme at virtually a moment's notice, and need therefore hold only small stocks. Since the production units are relatively small (furnace-machine-lehr-conveyor

belt; see fig. 11), the factory space taken up is also modest. The least versatile process is the one employing the ribbon machine. This machine is most suitable for the production of very large runs of bulbs of the same type. As a rule, their products cannot be directly assembled and finished on the same premises, and this means large stocks and considerable storage space, both in the glass works and in the lamp or valve factories.



Fig. 14. Eighteen-head machine for making bulbs from short sections of glass tubing. *A* housing for drive mechanism. *B* one of the 18 chucks, mounted on a horizontal, intermittently rotating turntable. *C* sectored rotor which, turning synchronously with the turntable, delivers tube lengths, one by one, from the magazine *D* into the chute *E*. *F* glass-inserting device. *G* chuck opener. The production cycle begins for each chuck at the position *I*, and ends at position *18*. *H* one of the air lines connected to each chuck for blowing the bulbs. *J* blow-mould. *K* shearing device. *L* chute into which the sheared bulbs fall. *M* chute for removing the "moil".

Machines for making bulbs from glass tubing

As mentioned above, machines designed for working molten glass cannot produce very small bulbs without involving a substantial loss of glass; small bulbs are usually made mechanically from glass tubing. In principle the process is as follows. A length of tubing of, say, one metre, the diameter of which is roughly equal to the neck of the bulbs to be produced, is sealed at one end and then, while it is rotating, heated over a certain length to a temperature at which it can be worked. When this temperature is reached, a blow-mould is closed around the heated part and air is blown into the tube. After the bulb thus formed has cooled sufficiently, the blow-mould opens and the bulb is severed from the tube. It is also frequently the practice to start from small lengths of tubing, which have been cut beforehand to the length needed for making one bulb.

It is evident that the rudimentary form of blowing technique involved here can only be applied if the maximum diameter of the bulb is not much greater than that of the tube. Otherwise, bulbs would be obtained whose wall at the position of the widest diameter would be much too thin. It is not possible to get around this difficulty by the use of tubing having a thicker wall or larger diameter, since the permissible diameter and wall thickness of the neck are rather narrowly restricted by the sealing technique used in the mechanical production of electric lamps. We shall return to this at the end of the article.

Before dealing with the latest machines for working glass tubing, we shall discuss in broad lines the design and operation of such a machine in the context of an 18-head machine for working short lengths of tubing, which can only produce bulbs whose bulb diameter is not much greater than the neck diameter.

An 18-head machine for working short lengths of glass tubing

In the Eindhoven 18-head machine³⁾, as in all machines for working glass tubing, a horizontal turntable which rotates about a vertical axis and carries round its periphery a number of chucks (in this case 18) is situated some 30 or 40 centimetres above the housing for the drive mechanism. Each of these chucks contains one of the lengths of tubing to be worked, mounted vertically. The turntable does not rotate continuously but in 18 equal steps, so that after each step a particular chuck occupies the

position of its predecessor. The chucks are in rotation, except in those positions where they are required to be stationary. The space between the top of the housing referred to and the turntable contains the burners and other equipment which together produce the bulb. A general view of the machine is to be seen in *fig. 14*, in which *A* is the housing for the drive mechanism and *B* one of the chucks.

The operations undergone by a piece of glass tubing in the machine are the following. First of all it is taken by the sectorised rotor *C* from the magazine *D* and propelled into the chute *E*. It is taken from the chute by the insertion device *F* (see also *fig. 18*), which inserts the glass from under into the chuck in position *I* (on left of turntable in *fig. 14*). In this operation, the chuck opener *G* rises and opens the chuck to receive the glass. The tube is now heated just above its base for a period corresponding to several turntable positions. The unheated part is then torn off by claws on the end of a vertically reciprocating spindle (see *fig. 15*). The tube thereby collapses and its lower end is reheated, the bottom being pushed in slightly by a rising rod to promote a neat sealed end. After further reheating at various

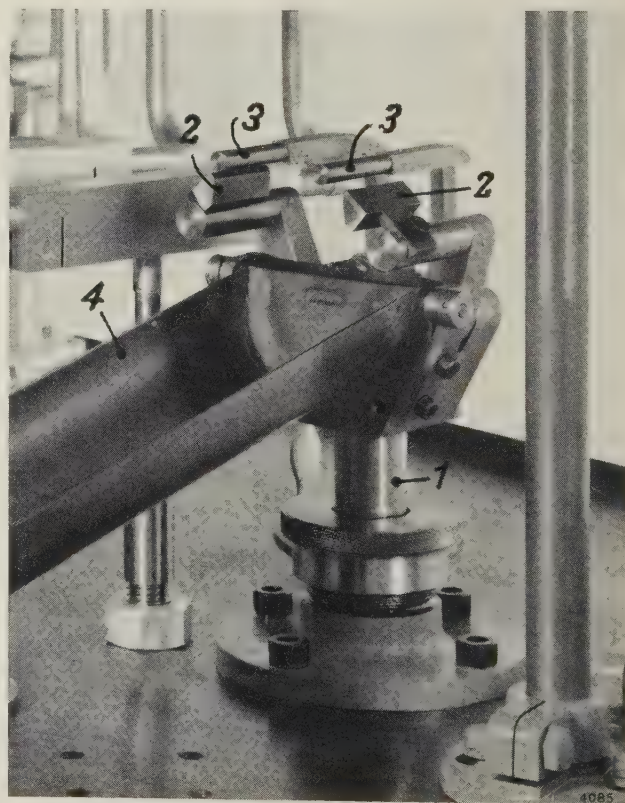


Fig. 15. The part of a glass-tubing machine where the tube is closed from underneath. 1 vertical reciprocating rod surmounted by tear-off tongs. 2 jaws of tongs. 3 stationary pins which, as the tube moves to the next station, break off the glass thread produced by the tear-off. 4 chute for discharging the torn-off piece of tubing.

³⁾ This machine was developed from a similar 12-head machine of Osram GmbH.

stations the tube reaches the (open) blow-mould. The mould closes around the tube and air is blown in (fig. 16). In the three following stages the bulb has time to cool, and finally it is severed from the upper portion (see *K* in fig. 14). It is discharged from

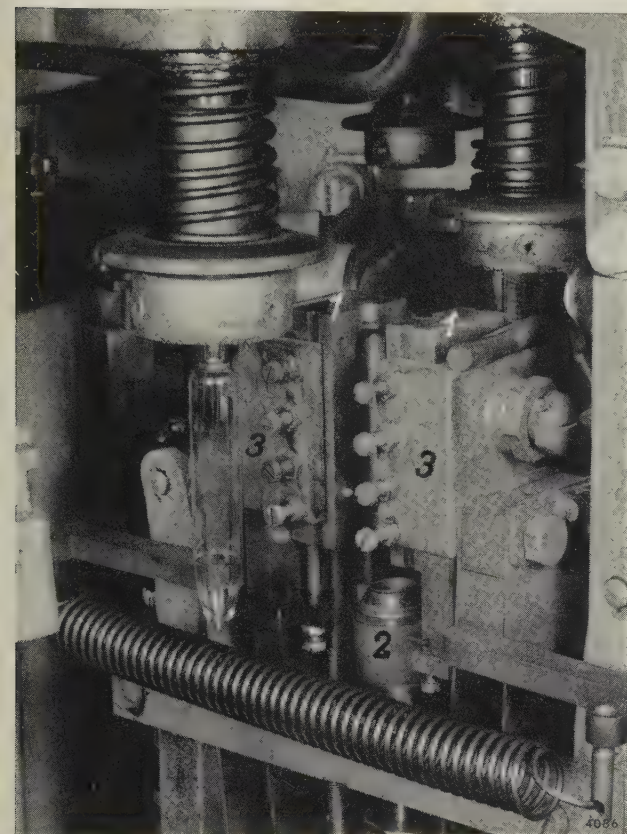


Fig. 16. Part of the 18-head machine showing a blow-mould. The mould shown here consists of three sections, i.e. two semi-cylindrical parts 1 which move towards each other horizontally to close, and a rising base 2. By unscrewing the bolts, the mould halves can be taken from the holders 3 and replaced by others.

the machine through the chute *L*. Upon reaching station 18, the chuck holding the remaining portion of tube is opened by *G* and the tube drops into the chute *M*. The chuck is now ready to receive a new charge in position 1.

The bulb that has now left the machine is not yet finished. The sharpness of the edges has to be removed by a fire-polishing process, and sometimes the end of the neck must be widened, tapered or flared, by a process known as flanging. These operations, like the conveyance of the bulbs from the blowing machine to the fire-polishing and flanging machines, may also be fully mechanized.

The method of producing the puff of air for blowing the bulb is illustrated in fig. 17a. Here 1 is the glass tube, the top of which is pressed into the

flared end 2 of a bushing 3, located above the jaws 4 of the chuck (all of which rotates together). Fitted in the flared top end 5 of the bushing is the nozzle of the air line 6 (*H* in fig. 14). This is effected in such a way as to leave a gap through which air can leak away during the blowing process. Varying the width of the gap provides a simple means of controlling the maximum pressure of the air.

It will be noted that the number of stations of the machine in a complete cycle — and thus the number of chucks — must at least be equal to the number of operations to be performed. Since the time spent at each station is obviously the same, protracted operations (particularly most heating processes) can better be distributed over several stations. Consequently the total number of stations is in practice two or three times greater than the actual number of operations.

Some comments on machines for working longer lengths of tubing

By suitably shaping the end of the line 6 (fig. 17a), the air-feed system described can also be usefully applied in machines for making longer sections of tubing. The end of the air line (see fig. 17b) is then contained *inside* the glass tube (which in this case projects some way above the chuck). Provided the sections are not unduly long, so that they can still be pushed into the chuck from underneath, a rigid

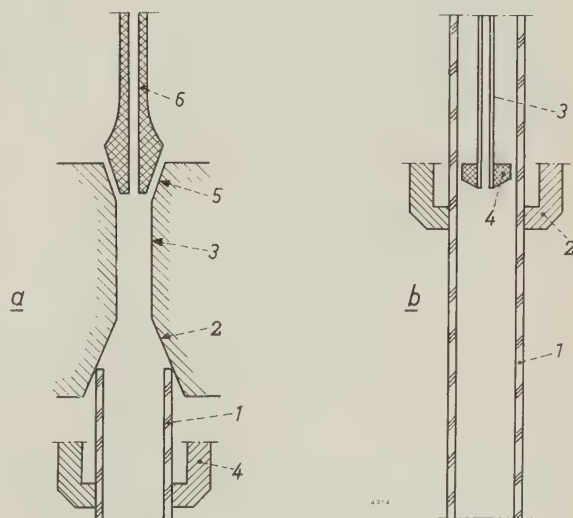


Fig. 17. Air feed for blowing the bulb in a glass-tubing machine. a) Method of feed in machines working short pieces of tubing. 1 top of glass tubing, pressed firmly into the flared bottom end 2 of the bushing 3 which, together with the clamp 4, forms part of a chuck. 5 flared top end of bushing. 6 air line inserted in 3 out allowing for some air leakage. b) Air feed system in machines for working long sections of tubing. 1 glass tubing. 2 clamp of chuck. 3 air duct with collar 4. Between this collar and the inside wall of the tube a gap is again provided to allow for air leakage.

air line may be used; in machines that handle tubing a metre long, a hinging point must be provided near the top of the line. The mouth of the air line is always as low as possible. For machines of this kind, this construction has considerable advantages over the

The chuck then closes again and the machine moves on to the next position. In some cases two glass-gatherers are fitted. During this operation the tubes are not in rotation. *Fig. 18a* shows the two glass-gatherers of a 32-head machine in course of develop-

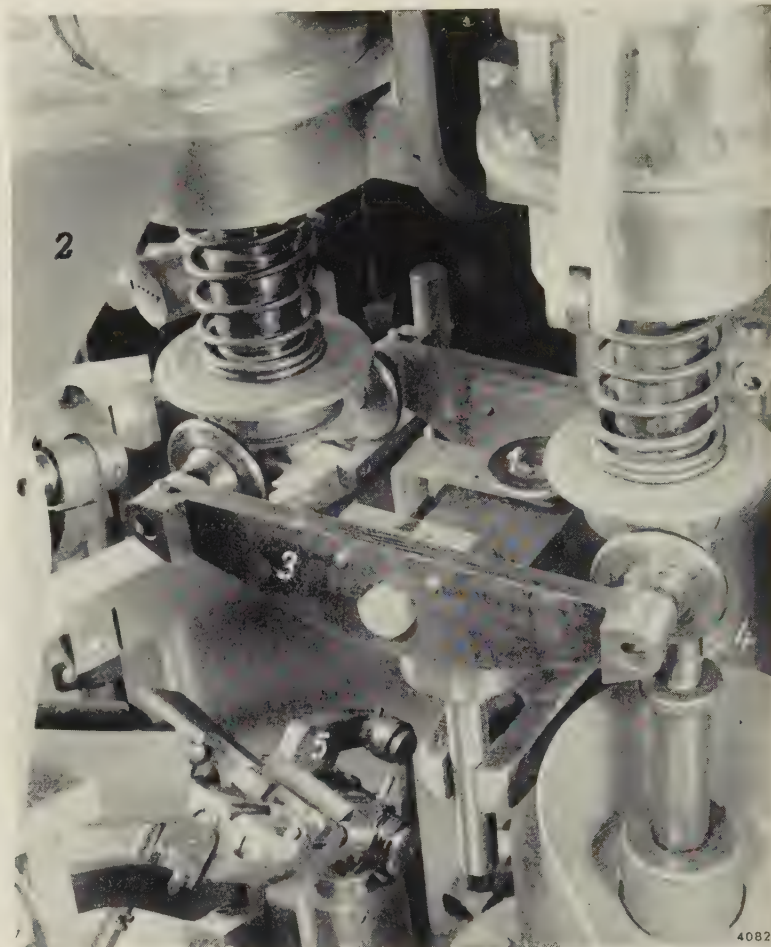
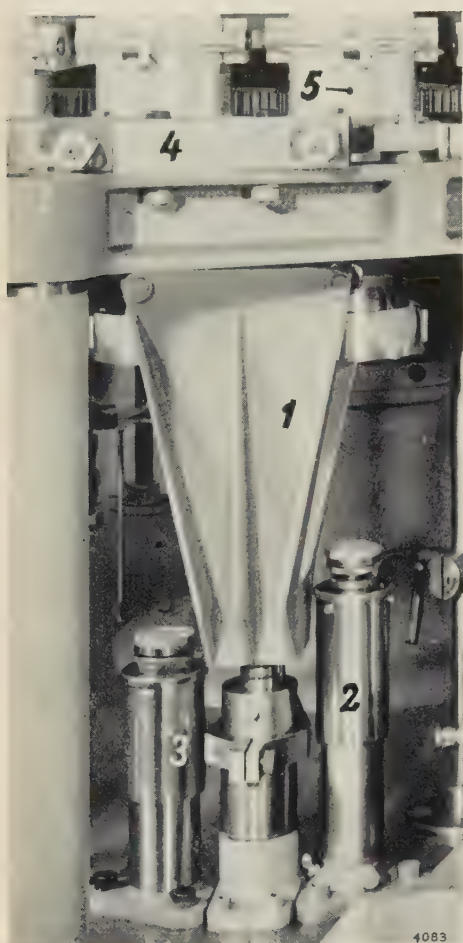


Fig. 18. a) Detail of 32-head machine for working long sections of glass tubing (in course of development). In the part shown, the tubes are being adjusted to the correct height. This is done here in two stages. 1 chuck opener. 2 first glass-gatherer. 3 second glass-gatherer. During the glass-gathering operations the chucks are not in rotation; this is achieved by the cam 4 actuating the lever 5.

b) Detail of a machine for working lengths of tubing from which more than one bulb can be made, but which are short enough to be inserted in the chuck from underneath. These machines are equipped with a feeler device 1 which signals the moment for delivering a fresh tube from the magazine 2. 3 chuck opener. 4 rod of glass-gatherer. 5 insertion device. (To make certain components visible, the valve heads were not in their working positions when this photograph was made.)

system whereby the air line (in this case a hose) has to be connected via a bung fitted in the end of the tubing (the Cleveland system).

In the machines for working long sections, each tube has to be moved up a bit after completing one cycle in its chuck, and for this purpose the machines are equipped with a so-called gatherer. This is a small plate mounted on a vertically movable rod, which takes up the tube as the chuck is momentarily released and carries it for some distance downwards.

In machines for working moderate lengths of tubing, and where the insertion process is identical with that in the machines for handling very short lengths, the insertion mechanism is fitted with a feeler device for ascertaining whether or not a tube has to be inserted (*fig. 18b*).

Machines without blow-moulds

For producing bulbs which are simple cylinders closed at one end (like many radio valves and

transistor envelopes), the use of a blow-mould may be dispensed with. In this case the starting point is tubing which has the diameter and wall thickness required for the bulb. After the tube has been closed by tear-off claws as described, the closed end is given the required shape by means of a *bottom mould*. The principle of this method is illustrated in *fig. 19*. In automatic machines equipped with a bottom mould,

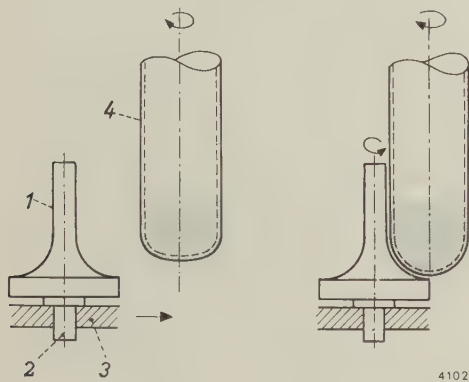
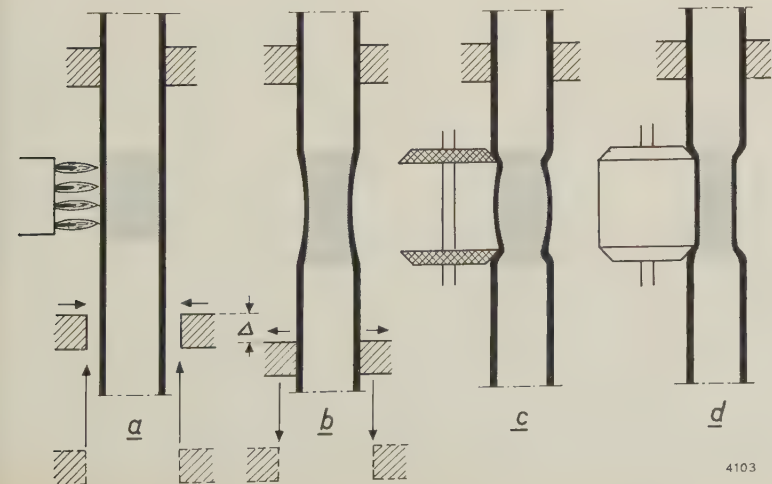


Fig. 19. Principle of making a cylindrical bulb with a “bottom mould”. The roller 1, which turns freely on a spindle 2 in the plate 3, is slowly moved towards the rotating glass tube 4 (already closed by the tear-off tongs) until its upper end abuts against the unsoftened part of the tube (the softened part is shaded). In this position a very gentle puff of air is blown into the tube, causing the bottom to follow the shape of the now rotating roller. Finally, the roller returns to its original position (shown on the left).

the small amount of air needed is admitted to the tube in the same way as described in *fig. 17*. The presence of a gap to allow air to leak away is especially important here. A too powerful puff, or thermal expansion of the enclosed volume of air, would have disastrous consequences in the absence of a blow mould.

Machines for making narrow-necked bulbs

Narrow-necked bulbs are made from tubing whose diameter lies between that of the neck and the bulb.



The required wall thickness and neck diameter are produced by the “*stretching and rolling process*”⁴⁾. The tube is heated at the place where the neck is to be, and as soon as the glass is soft enough it is stretched a little. With the tube rotating, the heated portion is then passed between three rollers to reduce it to precisely the required diameter. The wall thickness of the rolled part which, without stretching, would be greater than that of the original tubing, can be controlled by varying the degree of elongation. The manner in which this stretching and rolling process takes place in the machine under development at Philips is represented schematically in *fig. 20*. The most characteristic features are 1) the fact that the tube is clamped only momentarily *under* the heated part for the purpose of stretching, but is otherwise freely suspended (apart from its enclosure between three centring rollers during the rolling process), and 2) the fact that the rolling process takes place in two stages, which improves the precision. Because of the fact that the tubes are not clamped from underneath, the design of the machine need not be essentially different from that of the 18-head machine described above. This leaves considerable freedom for the positioning of the burners and allows the mechanism for closing the blow-moulds to be simpler than is possible in machines equipped with two rotating turntables each carrying rotating chucks (one for the top and one for the bottom of the tubes). To enable the entire production process, including the stretching and rolling, to be carried out on a single machine, the number of stations was increased, as mentioned in *fig. 20*, to 32.

A view of the relevant part of the new machine is shown in *fig. 21*. Various details are explained in

⁴⁾ This principle has long been used in machines for making ampoules, and has also been applied for making bulbs (E. Mickley and M. Thomas, *Glastechn. Ber.* **26**, 197, 1953).

Fig. 20. Stages of the *stretching and rolling* process in the 32-head machine. The part to be stretched is first heated (shaded). When it is hot enough, a chuck rises, grips the tube from underneath and stretches it over the required elongation Δ . The chuck then opens and drops back to its original position, enabling the tube to move to the next position (*a* and *b*). The hot part is now indented by two wheels, which accurately define the section to be rolled (*c*), and finally, possibly after reheating, it is rolled to the required diameter (*d*).

the caption. As regards the centring rollers (8) it should be noted that they are not driven but are set in motion by the tube itself. The tube must not be too hot at the rolling position, otherwise there is a danger of it twisting. The rollers themselves are very light and rotate very easily.

The 32-head machine differs somewhat from the other in various points of construction. The housing consists of a lower section fitted with vertical ventilation vents at the sides. The gas, air and oxygen lines, and various valve assemblies (three for each burner) are mounted here at the height of the upper section. The motors and drive mechanism are all in the lower section of the housing. All that the upper section contains,

glass. Depending on the type of bulb produced, the capacity of the 18-head machine first described varies between 1000 and 1600 bulbs an hour. Roughly the same figures hold for the later-developed variants of this machine. The 32-head machine now under development has already proved itself capable of a production rate of 1600 bulbs an hour. This is expected to be improved on in the near future.

Choice of production method

A point already mentioned in passing, and which the bulb manufacturer always has to decide, is which method of production is to be preferred. We have

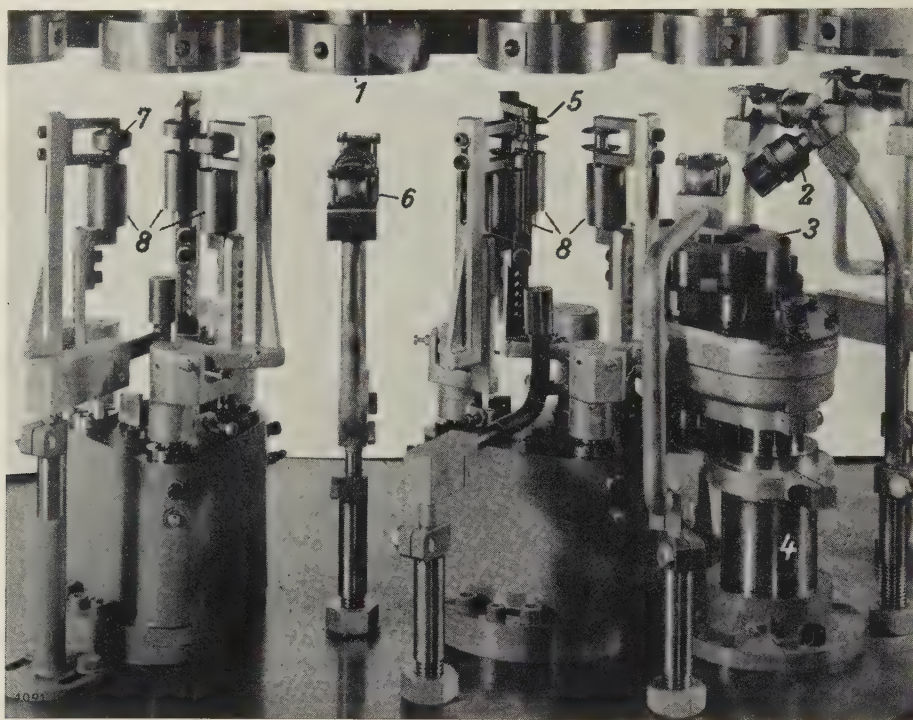


Fig. 21. Part of the 32-head glass-tubing machine where the stretching and rolling process takes place. 1 one of the six chucks visible. 2 one of the burners. 3 chuck on vertically reciprocating rod 4 for stretching. 5 indenting wheels (for the first stage; see fig. 20). 6 burners for reheating. 7 roller for second stage. During the rolling process the lower part of the tube is centred by the rollers 8.

apart from various vertical shafts and rods, are hoses leading from the valves to the burners. This construction makes it possible to adjust or replace the cams of the drive mechanism without having to remove the valves (the cams are designed so that they can be replaced without taking the shaft out of its bearings). Moreover, because of the use of hoses instead of metal pipes for the connections between valves and burners, it is possible to change quickly and simply a gas-air burner, for example, into a gas-oxygen burner. The ventilation obviates the risk of explosions resulting from any slow leakages.

A selection of bulbs mechanically produced from glass tubing is to be seen in fig. 22.

The production capacity of the machines for working glass tubing is somewhat lower than that of the earlier discussed machines that work molten

seen that in a few cases production by hand leads to the lowest production costs, and also that, by mechanized methods, large bulbs can on the whole be made more cheaply from molten glass and small ones more cheaply from glass tubing. In this connection, glass losses were shown to be a very important factor. Cylindrical bulbs for radio valves, for example, can be made most economically from glass tubing, the glass loss then being very small.

We shall now examine these rough indications in more detail and expand on them. Closer consideration is especially important where the best method of production is to be decided for making bulbs that are neither large nor very small, e.g. a car headlamp bulb,

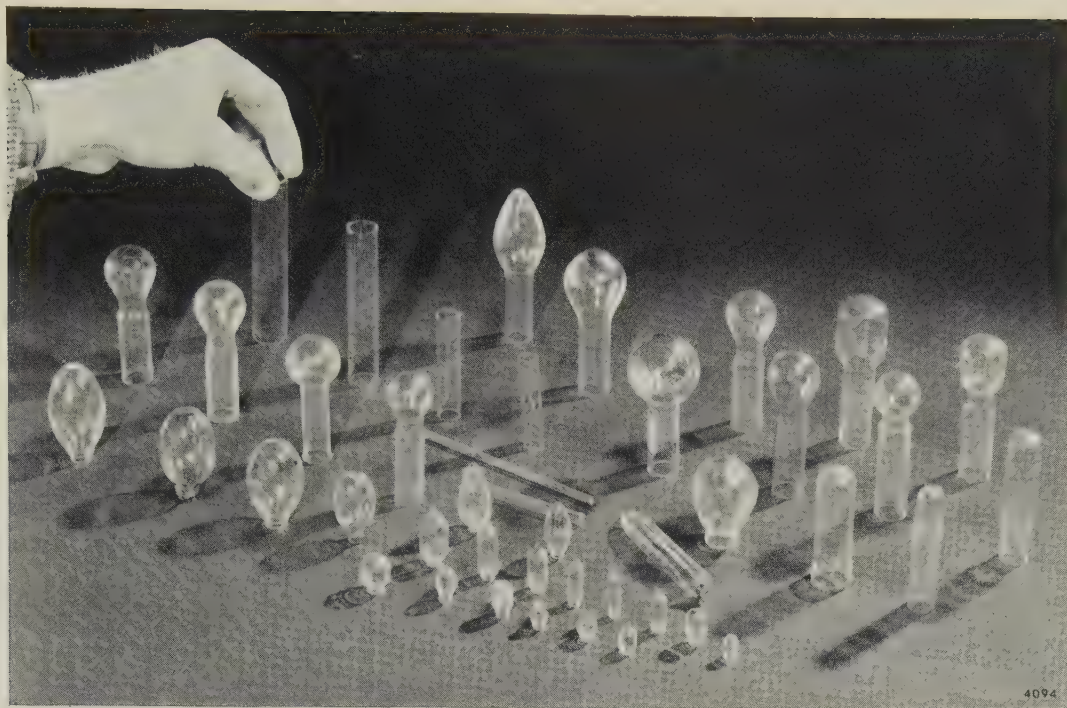


Fig. 22. A selection of bulbs mechanically produced from glass tubing.

The first factor to be considered is the size of the production run. If this is small, production from glass tubing will generally be more advantageous, provided at least that glass of the required kind and dimensions is in stock. There is then no need to start up a glass furnace for this specific purpose. If the manufacture can be combined with that of other bulbs of similar dimensions and the same type of glass, economic production is also readily possible with the Eindhoven 16-head machine for working

molten glass, this machine being capable of turning out different models at the same time.

The glass loss is governed not only by the weight of the bulb but also by the shape of the neck. This is bound up with the various methods by which the mount, which carries the filament, is later to be sealed to the bulb in the lamp factory.

For the first method, called the "drop-seal" process and represented schematically in *fig. 23a*, the bulb on leaving the glassworks must have a

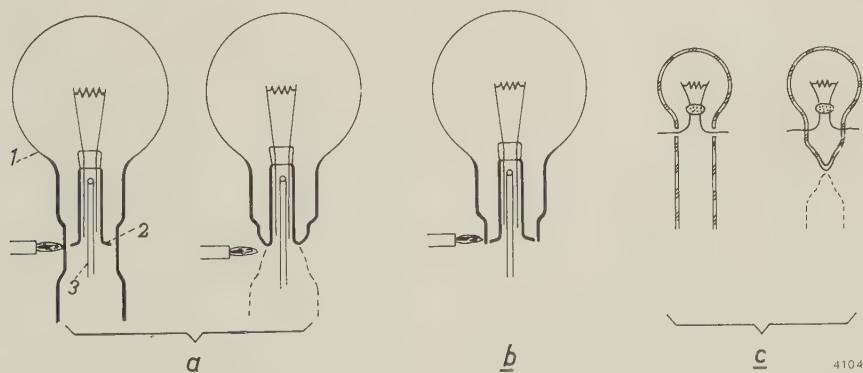


Fig. 23. The various methods by which the mount, which carries the filament, is sealed to the bulb in the lamp factory.

a) Drop-seal process. Here the bulb from the glassworks (left-hand sketch) has a longer neck than the lamp to be made from it. After the bulb (1) and the tapering bottom end (2) of the mount (the "flare") are sealed together, the bottom section of the bulb (dashed line in the right-hand sketch) is burnt off. The gap between flare and neck is here fairly wide. The tube 3 is the pump stem.

b) Rim-seal process. The bulb here is cut to the definitive length and the gap between neck and flare must be narrow.

c) Butt-seal process. Here too the bulb neck is short. A butt-seal is made with a tube having the same diameter as the neck; after evacuation the tube is sealed off close below the butt-seal. The lead-in wires are incorporated in the butt-seal.

considerably longer neck than the electric lamp to be made from it. The neck must also have a large enough inside diameter for it to fit with a wide clearance around the stem. After the mount, carrying the filament assembly, has been properly positioned inside the bulb, the whole is rotated and the bulb is heated around the bottom of the mount. As soon as the glass softens, the neck becomes gradually constricted and finally touches the "flare" of the mount. Further heating fuses the two together. The bottom part of the neck is then burnt off by positioning the flame somewhat lower, in which process it may be pulled with tongs or allowed to sag under its own weight.

In the "rim-seal" process the neck of the bulb leaving the glass works is just as long as required for the finished lamp, and its inside diameter is such that the flare of the mount fits it fairly exactly. The rim of the neck and of the mount are brought into alignment and sealed together (fig. 23*b*).

A favourable feature of the drop-seal method is the fact that the neck diameter may vary between fairly wide limits. The fact that the bulb wall immediately above the seal may be fairly thin — as a result of elongation — is sometimes, though not usually, a drawback. The rim-seal process produces stronger seals, but fairly strict demands are imposed on the roundness of the bulb necks, of the spread in their diameter and on the constancy of the wall thickness in the sealing zone. The same applies to the cleanliness and soundness of the edges of bulb and flare. In the rim-seal process the clearance between neck and flare is required to be small, whereas in the drop-seal process the opposite is the case, since a small clearance would result in a thick glass rim around the fusion zone and increase the risk of cracking.

The third method, called the "butt-seal" process (fig. 23*c*), also uses a short-necked bulb. A tube of the same diameter is butt-sealed to the neck and, after evacuation, burnt off a short distance below the seal. In this case the lead-in wires are fused into the joint.

Turning now to the economy of the various bulb-blowing machines, it is found that, in the lighter ranges, production from molten glass can compete longest with the glass-tubing method provided the

drop-seal process is used. Apart from the difference in glass losses, production from molten glass is in the disadvantage if other methods of sealing are applied, in view of the finishing (burn-off) operation then required, which considerably increases the production costs. Moreover, the necks of bulbs produced from glass tubing better conform to the above-mentioned requirements of constant wall thickness, etc., for the rim-seal process. This is especially the case where stretching and rolling is involved.

Apart from the above considerations, which are primarily of an economic nature, the manufacturer has various other factors to take into account. For example, the choice between production from molten glass or from glass tubing is sometimes influenced by the type of glass required. In this case, the glass-tubing machines have the advantage; the mechanized production of hard-glass valves, for instance, presents difficulties if molten glass is used. The quality and finish of the bulbs are also, of course, factors that carry some weight. As regards finish, bulbs made from molten glass are definitely superior. This also applies to the smaller models, which cannot be made without some loss of glass. In so far as the strength and distribution of the wall thickness are concerned, it should be mentioned that the bulbs, both large and small, made on the Eindhoven 16-head machine are entirely satisfactory. In this respect, however, bulbs made from glass tubing are scarcely, if at all, inferior to the others if the production involves a stretching and rolling process.

Summary. Machines for producing lamp bulbs or valve bulbs are designed for working either molten glass or glass tubing. Of the first category the author discusses the ribbon machine, the vacuum-and-blowing machine and a machine, developed at Eindhoven, which operates without glass loss. The latter is a continuously rotating machine equipped with 16 blowing units. Each unit is capable of turning out a different model, subject only to the limitation that the amount of glass used for each is the same. The production capacity is about 4000 an hour. Since very small gobbs cool too quickly to be worked with such machines, small bulbs are made from glass tubing. In this category an 18-head machine is discussed, also developed at Eindhoven, which handles short lengths of tubing. Some variants are then described, including machines that work long lengths of tubing and machines using a bottom mould instead of a blow-mould. Their production capacity ranges from 1000 to 1600 bulbs an hour. Mention is made of the production of narrow-necked bulbs from glass tubing by a process of stretching and rolling. The last section is devoted to the economic and other factors governing the choice of machine.

TESTING OF MATERIALS FOR GLASS-TO-METAL SEALS BY MEANS OF STRESS BIREFRINGENCE

by J. de VRIES *).

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One of the principal causes of stresses in glass-to-metal, glass-to-ceramic or glass-to-glass seals is the difference in thermal expansion between the sealed materials. Since the stresses must not become so high as to cause the glass to crack, it is important to have some method of checking beforehand the expansion of the materials to be used, in order to avoid difficulties during production. In many laboratories and factories it is still common practice to measure the expansion directly as a function of temperature with a dilatometer and to compare the resultant curves. A single expansion coefficient, derived from the dilatometer curve, is sometimes used to specify a material in a simpler (though less adequate) way.

Now that the marked increase in industrial production in Europe is giving rise to closer international cooperation in the field of glass processing, it is becoming more and more apparent that the dilatometric method is not accurate enough. It therefore seems desirable to draw attention once again to the stress-birefringence method of measuring the relative expansion. This method, in which the stress is deduced from the birefringence (double refraction) in test seals of standard shape, has been applied at Philips for more than twenty years, and was described in this journal in 1947 ¹⁾. To avoid unnecessary repetition, we shall lay particular emphasis here on glass-to-metal seals, which were only touched on in passing in the 1947 article.

The stress-birefringence method

The birefringence is measured on a test seal of one of the shapes illustrated in *fig. 1*. In order to compare glass samples, or samples of glass and ceramic, small plates of these materials are fused together (*fig. 1a*). For the fusion of sheet metal and glass the so-called plate seal in *fig. 1b* is used; the cylindrical form in *fig. 1c*, the bead seal, is appropriate where metal wire is concerned. If the diameter of the wire is greater than 3 mm (in which case it can better be referred to as a rod), a flat edge is ground on the rod to which a plate seal is then made. Various examples of such test seals are shown in *fig. 2*.

If the fused materials have different coefficients of expansion, stresses will arise upon cooling. Cooling

the samples in an annealing oven ensures that the residual stresses are due solely to the difference in the expansion of the two materials. It is well known that stresses in glass cause double refraction ²⁾. The intensity of the birefringence, expressed in optical path difference per cm thickness of the birefringent

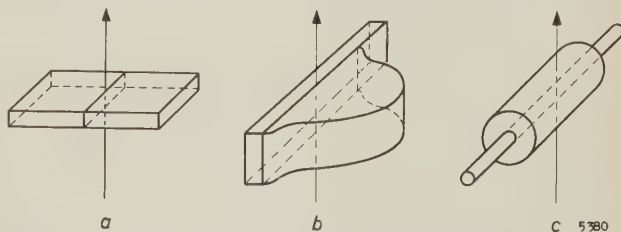


Fig. 1. Standard shapes of test seals for determining expansion differences by the stress-birefringence method. Polarized light is passed through in the direction of the arrows. Shape (a) serves for glass joints and glass-to-ceramic seals, sometimes also for metal and glass, (b) for plate-type glass-to-metal seals, and (c) for the fusion of metal wire and glass (bead seals).

material, is a measure of the stress, and hence of the difference in expansion. The optical path difference is measured in $m\mu$ with the aid of polarized light, the intensity of the birefringence thus being given in $m\mu/cm$.

It may be useful to recall briefly the principle of birefringence. If a plane-polarized electromagnetic wave falls perpendicularly on a birefringent plate, the wave is split into two components polarized in directions at right angles to one another. These components are distinguished by a somewhat different velocity of propagation, so that the original wave front splits into two wave fronts. After passing through the plate, the two wave fronts show an optical path difference which is proportional to the thickness of the plate, provided the birefringence in the plate is constant over the entire thickness.

In test seals using a glass plate (*fig. 1a* and *b*) the light is incident perpendicular to the plate and the optical path difference is measured on the light ray passing close to the interface, where the stress — and optical path difference — is greatest. The latter is then divided by the thickness of the plate.

When comparing the results obtained on various plate seals (*fig. 1b*), it must be remembered that the stress for a given glass-metal combination is smaller the thinner the metal. This is due to the fact that a thin piece of metal can more easily deform and thus relax the stresses. The effect is noticeable in metal

*) Glass Division, Eindhoven.

¹⁾ A. A. Padmos and J. de Vries, Stresses in glass and their measurement, Philips tech. Rev. 9, 277-284, 1947/48.

²⁾ See e.g. J. Partridge, Glass-to-metal seals, Society of Glass Technology, Sheffield 1949.



Fig. 2. Various test seals. Top left: glass-to-glass, viz. translucent, opalescent and black glass sealed to translucent glass. Top right: bead seals. Bottom left: glass-to-ceramic. Bottom right: plate seals. Roughly actual size.

plates thinner than about 0.5 mm. Results for thin plates are therefore reduced to those for thick plates by applying corrections established experimentally.

In bead seals the light is directed on to the seal perpendicular to the metal wire, and the optical path difference is measured for a light ray tangential to the metal wire. In this measurement the bead is placed in a glass cell containing a liquid which has practically the same refractive index as the glass. This avoids the complication of reflection and refraction at the surface of the cylinder. The measured optical path difference is divided by the distance covered by the light ray through the bead (i.e. by the distance A_1A_2 in fig. 3) and a result is again obtained in $m\mu/cm$.

In bead seals the result found for a given combination of glass and metal depends on the ratio between the diameters of bead and wire. To obtain comparable figures it is therefore necessary to reduce the results to one particular ratio; the ratio 3 is commonly used. For this purpose, Hull and Burger have worked out a graph on the basis of a theory put

forward by Poritsky^{3) 4)}. For example, where the measurement concerns a bead seal in which the ratio of the diameters is 4, it follows from this graph

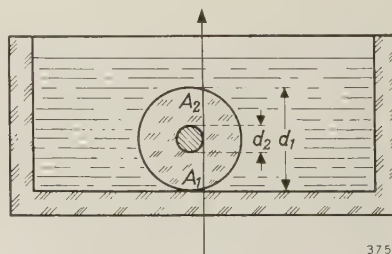


Fig. 3. For measuring the stress birefringence in a bead seal, the optical path difference for a light ray tangential to the metal wire is divided by the distance A_1A_2 through the bead. The bead is immersed in a liquid having almost the same refractive index as the glass in the seal.

³⁾ A. W. Hull and E. E. Burger, Glass-to-metal seals, *Physics* **5**, 384-405, 1934.

⁴⁾ H. Poritsky, Analysis of thermal stresses in sealed cylinders and the effect of viscous flow during anneal, *Physics* **5**, 406-411, 1934.

(fig. 4) that the result must be divided by 0.7 in order to reduce it to a ratio of 3⁵).

It is sometimes necessary to compare results obtained on plate and bead seals. Obviously, a direct comparison is not possible, and in this case, too, correction factors must be applied that are determined by experiment.

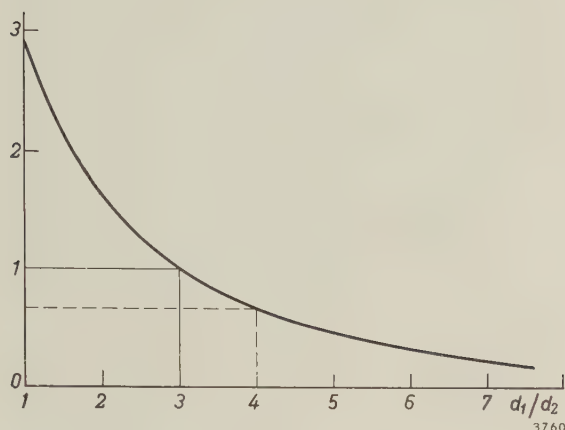


Fig. 4. Hull and Burger correction graph³⁾ for comparing measurements on bead seals having different ratios of bead diameter d_1 and wire diameter d_2 . A result obtained for $d_1/d_2 = 4$ is divided by 0.7 to reduce it to the result for $d_1/d_2 = 3$.

Standard glasses

An important advance has been the introduction of standard glasses. A particular batch of glass is reserved for test purposes and thereby ranked as a standard glass with which other materials are compared by means of the test seals shown in fig. 1. In this way, expansion values are found which can be compared one with the other.

For any given type of glass, i.e. soda-lime glasses, lead glasses, borosilicate glasses, etc., a standard glass of the same type is required. The various metals appropriate for sealing to each particular type of glass are tested with respect to the standard glass of the same type. Standard glasses are given code numbers, e.g. 28/4, and the expansion of the investigated materials is expressed for brevity as, for example, T50 m μ /cm in 28/4 (T means a tensile stress in the standard glass), or C100 m μ /cm in 28/4 (C means compressive stress in the standard glass).

A distinction is made between *basic* standard and *secondary* standard glasses. A secondary standard is for regular use. When the supply is exhausted, glass

from a fresh batch is taken as the secondary standard. The secondary standards, which are all given their own code numbers, are chosen to compare as closely as possible with the basic standard. The latter is used only for the purpose of selecting fresh secondary standards and for determining any corrections that may be necessary to the measurements made with the secondary standards. In this way, stress values are obtained which can immediately be compared one with the other, even though years may have elapsed between the tests, for all values are expressed in stresses relative to the same basic standard.

Comparison of the stress-birefringence and dilatometric methods

The stress-birefringence method gets around one principal drawback of the dilatometric method, which is that a relatively *small* difference between two quantities has to be deduced by measuring the quantities themselves and subtracting one from the other. The stress-birefringence method is therefore much more accurate and, moreover, quicker and simpler. A theoretical advantage of the dilatometric method is that the results are in principle independent of the method of measurement. The results obtained in the different laboratories should thus be directly comparable, whereas the results of the stress-birefringence method are comparable only in so far as identically made test seals and identical standard glasses are used. In practice, however, the extent to which dilatometric results can be compared has proved to be very disappointing, so that the advantage is really illusory.

An advantage of the stress-birefringence method, not yet mentioned, is its close relevance to practice, i.e. to actual seals. For tracing the causes of rejects, and in the search for better methods of production and control, the stress-birefringence measurements provide much more assistance than dilatometric measurements. An example will be discussed at the end of this article.

The wider adoption of the stress-birefringence method calls for close cooperation between all parties concerned. Such cooperation, on an international level, promoted by the Physics Laboratory of the Philips Glass Development Centre, is gradually gaining ground.

Expansion tolerances for glass and metal

Suppose that a glass G and a metal M are sealed together in a certain product. As regards their expansion, G and M are of course chosen to match, but there is always a certain spread in the values of

⁵⁾ In certain cases, where the delayed elasticity (elastic after-effect) of the glass plays a part, the Hull and Burger graph leads to false conclusions. This subject is dealt with in detail by A. L. Zijlstra and A. M. Kruithof, L'élasticité différée d'un verre borosilicate et son influence sur la formation de contraintes dans des scelllements de ce verre, Verres et Réfractaires 12, 127-141, 1958.

the actual expansion coefficients. In unfavourable cases, i.e. where the expansion of the glass is on the high side and that of the metal on the low side — or vice versa — the glass may therefore be in danger of cracking. The question to be decided is what tolerances must be specified for the expansion of glass and metal separately in order to be sure of a good joint.

To answer this question, it is necessary first of all to know what *differences* in expansion are permissible. In a few cases it is possible to discover this systematically by making a test run of the product concerned using materials with increasing differences in expansion. That is the ideal method, but in the factory it is seldom practicable. As a rule a reject analysis has to be resorted to. The glass and metal of a cracked specimen are taken and used to make a test seal. Depending on the shape of the metal (sheet or wire), this may be a plate or a bead seal. The measured difference in expansion is evidently impermissible for the product in question. By investigating a series of cracked specimens in this way, an assessment can be made of the differences in expansion (expressed in $m\mu/cm$) that may be tolerated for the product. (At this stage, then, a standard glass is not used.)

The next step is to draw a graph in the following way. A test seal is made of a sample G_1 of glass G , to the corresponding standard glass S . Let the birefringence measured in S be g_1 $m\mu/cm$. A test seal (plate or bead) is also made of G_1 to a sample M_1 of the metal M . Let the birefringence measured in G_1 be a_1 $m\mu/cm$. The points g_1 and a_1 are now plotted on the abscissa and ordinate, respectively, of a graph, defining the point A (see fig. 5). In the same way we deal with a second glass sample G_2 which shows a slightly different expansion, e.g. because it

comes from a different batch, and we find point B . (In both cases the same metal sample M_1 is used.) Other glass samples yield points which all lie virtually on the straight line AB , so that in principle we need only establish two points. The straight line AB is thus characteristic of the metal sample M_1 . Other metal samples (showing a somewhat different expansion) yield lines parallel to AB . The points at which these lines intersect the vertical axis obviously represent the stresses to which these metal samples give rise in the standard glass.

We can now proceed to specify the expansion tolerances for the glass and the metal separately. In this connection we have some freedom of choice, in that the tolerance for the glass will be wider the closer we make the tolerance for the metal, and vice versa. Assume for example that it is desirable for certain reasons to specify for the metal an expansion corresponding to between C50 and C190 in S . We now draw lines in fig. 5 parallel to AB through the points C50 and C190 on the ordinate (where the birefringence in S is zero, i.e. the expansion of the glass G is identical to that of S). Suppose that reject analysis has shown the permissible differences in expansion between G and M to lie between C220 and T50 in a standard test seal. Horizontal lines corresponding to these values yield the points of intersection P and Q (see fig. 5). The abscissae of P and Q then represent the required tolerances for the glass G , namely T43 and C100, or, in round figures, T50 and C100 in S .

Quality control based on stress-birefringence measurements

To conclude this article we shall consider an example of the assistance afforded by stress-birefringence measurements in tracing and removing the causes of fracture. The example in question concerns the transmitting tube shown in fig. 6. This contains a fernico ring A , to one side of which the glass envelope B is sealed, and to the other the glass cap C . Under certain conditions during operation the ring A may be heated by eddy currents to above 200 °C, as a result of which repeated cracking occurred in the neighbourhood of the seal between the envelope B and the ring A . The plane of fracture was always found to lie roughly parallel to the plane of the seal.

Stress-birefringence measurements of the expansion difference as a function of temperature were made on plate-type standard seals between glass and metal taken from tubes which had fractured. Curves such as curve 1 in fig. 7 were obtained. For recording “polarimeter” curves of this kind, the test

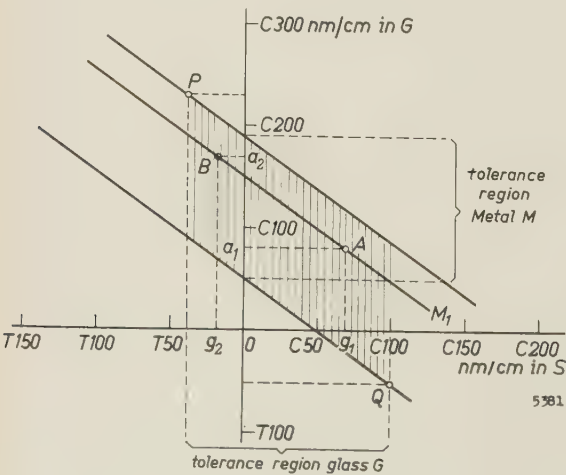


Fig. 5. Graphic determination of the expansion tolerances for glass in a glass-to-metal seal where the tolerances for the metal are given, or vice versa. (1 nm = 1 nanometer = 1 $m\mu$.)

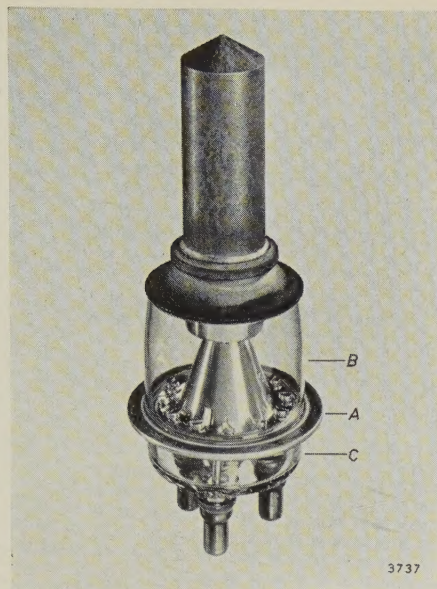


Fig. 6. A transmitting tube where the cause of fracture near the seal between the glass envelope *B* and the fernico ring *A* was traced and removed with the aid of stress-birefringence measurements on standard test seals. *C* is a glass cap sealed to the other side of ring *A*. Height of the tube approx. 20 cm.

seal is heated in a small oven specially designed for the purpose. The remarkable shape of the curves is due to the non-uniform expansion of both glass and metal ⁶⁾.

It can be seen that a maximum tensile stress prevails in the test seal at 200 °C. This does not imply that the same stress will be present in the actual tube seal; the conditions in the actual seal are never exactly the same as in the test seal, and this again has its effect on the stresses. Nevertheless, the peak at 200 °C in the polarimeter curve does give reason to suppose that excessive expansion of the metal in relation to the glass is the cause of the trouble experienced. Since the heat is generated in the metal ring, this will be hotter than the glass,

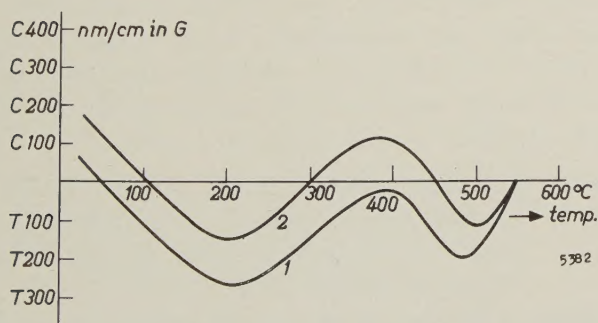


Fig. 7. Birefringence as a function of temperature (so-called "polarimeter" curves), for a standard glass-to-metal seal made with the glass and metal used in the tube type shown in fig. 6.

⁶⁾ The irregular expansion of fernico, which is due to the magnetic properties of this alloy, is turned to advantage for ensuring that, with an appropriate glass, the difference in expansion fernico-glass as a function of temperature does not become excessive.

and this will accentuate the higher expansion of the metal. Suppose that at room temperature there are virtually no stresses present (fig. 8*a*). At higher temperatures a deformation as sketched in fig. 8*b* will then occur. This would be accompanied by a tangential tensile stress together with an axial compressive stress on the inside, and an axial tensile stress on the outside of the fusion zone. If the latter stress is responsible for the rupture, it should be possible to remove the trouble by using only such combinations of metal and glass for which the polarimeter curve is somewhat higher, e.g. such as curve 2 in fig. 7. It was found that this measure indeed produced the expected result. At room temperature a tangential compressive stress will now prevail in the glass, together with an axial compressive stress on the outside of the fusion zone and

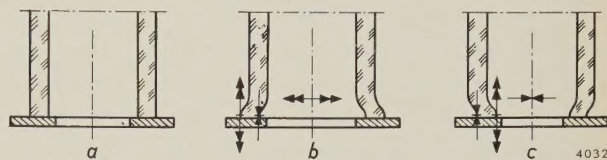


Fig. 8. Illustrating the cause of fracture in a seal between the envelope *B* and the fernico ring *A* as in fig. 6, and the corrective measure adopted. It is assumed that in a glass-to-metal seal to which curve 1 in fig. 7 applies, no or hardly any deformation, and hence no stress, is present at room temperature (*a*). The deformation that then occurs at higher temperature is shown in (*b*). Tensile stresses are denoted by double arrows, compressive stresses by single arrows. In a glass-to-metal seal to which curve 2 in fig. 7 applies, the seal is pre-stressed at room temperature (*c*).

an axial tensile stress on the inside. When the tube is switched on, this tensile stress will decrease, whilst the compressive stress on the outside will only change to a tensile stress at elevated temperatures; this stress, however, can now no longer assume a value capable of causing fracture. At room temperature the glass seal is now pre-stressed. The pre-stress must not, however, be unduly large, otherwise the tensile stress prevailing on the inside of the seal at room temperature and below, e.g. during transport, may prove dangerous. The limits within which the polarimeter curves must lie have been established by experiment.

Summary. A sensitive, simple and quick method of checking the relative expansion of glass-glass, glass-metal or glass-ceramic combinations is to measure the stress birefringence, i.e. the double refraction, in standard-shaped test seals of the materials concerned against a suitable standard glass. The large-scale adoption of this method instead of the still commonly used but less satisfactory dilatometer tests calls for close cooperation between the relevant industries. International cooperation is gradually increasing in this field. The article gives a description of the stress-birefringence method in comparison with the dilatometric method, and discusses the graphic determination of expansion tolerances for glass and metal in a given seal. It concludes with an example of the application of stress-birefringence measurements in tracing and eliminating the causes of fracture in a particular product.

ABSTRACTS OF RECENT SCIENTIFIC PUBLICATIONS BY THE STAFF OF N.V. PHILIPS' GLOEILAMPENFABRIEKEN

Reprints of these papers not marked with an asterisk * can be obtained free of charge upon application to Philips Electrical Ltd., Century House, Shaftesbury Avenue, London W.C. 2, where a limited number of reprints are available for distribution.

2806: C. G. J. Jansen and A. Venema: A McLeod manometer with prescribed volumes for use as a standard instrument (Vacuum 9, 219-230, 1959, No. 3/4).

The McLeod gauge is one of the few instruments with which it is possible to measure the actual values of low gas pressures ($5 \cdot 10^{-5}$ mm Hg) without changing the composition of the gas. The McLeod gauge is therefore indispensable for calibrating the faster indicating instruments which only register relative pressure units, e.g. ionization gauges, heat-conductivity manometers, etc. Since it is very cumbersome to make and calibrate a McLeod gauge that can be used as a standard, it is worth while to improve the construction in such a way that a calibration can be omitted. In connexion with this problem a critical study was made of the formulae used to calculate the gas pressure from the readings of the McLeod gauge, which lead to expressions for the relative systematic and random errors limiting the measuring accuracy. By using a very accurate set of jigs in making the capillaries and the transition volumes at the connexion between capillaries of different diameters, and by addition of a small correction volume to the compression bulb, it was possible to construct a McLeod gauge indicating the actual gas pressures in the range of 3.5 to 10^{-5} mm Hg on one convenient set of scales. The volume of the compression bulb and the volume and diameters of the capillaries were calculated in such a way that full centimetres on the various scales correspond to 10^{-3} , 10^{-2} and 10^{-1} mm Hg, respectively. The zero lines of the different sub-ranges of the instrument lie at whole centimetres from each other and at multiples of half-centimetres from the top of the compression capillary.

2807: W. L. Wanmaker and C. Bakker: Luminescence of copper-activated calcium and strontium orthophosphates (J. Electrochem. Soc. 106, 1027-1032, 1959, No. 12).

Copper produces a strong luminescence in $\text{Ca}_3(\text{PO}_4)_2$. Luminescence in $\text{Sr}_3(\text{PO}_4)_2$ occurs only in the presence of small amounts of foreign ions, such as Ca, Zn, Cd, Mg, or Al. These additions give rise to a new crystal phase which is probably isomorphous with $\beta\text{-Ca}_3(\text{PO}_4)_2$. The emission peaks of $\beta\text{-Ca}_3(\text{PO}_4)_2$, $\alpha\text{-Ca}_3(\text{PO}_4)_2$, and of $\text{Sr}_3(\text{PO}_4)_2$ modi-

fied with Al, under excitation with 2537 \AA , are found at 4800, 5700, and 4950 \AA , respectively. Sensitization occurs with Mn, giving rise to a red emission peak. The fluorescence intensity remains good up to quite high temperatures ($\sim 300^\circ\text{C}$), especially that of $\beta\text{-Ca}_3(\text{PO}_4)_2\text{-Cu}$ and $\text{Sr}_3(\text{PO}_4)_2$ partly substituted with Mg and Ca. The application of these phosphors in lamps presents some difficulties due to the materials' sensitivity to air at binder bake-out temperatures.

2808: H. Bremmer: Méthodes mathématiques appliquées dans la théorie de la propagation des microondes (Conferenze del Seminario di Matematica dell'Università di Bari, March 1959, Nos. 45 and 46; publisher N. Zanichelli, Bologna 1959). (Mathematical methods in the theory of microwave propagation; in French.)

The first part of this article shows how the propagation of radio waves through the troposphere is influenced by local turbulences and by the presence of regions (of mainly horizontal extent) of differing refractive index. In the first case a role is played by the autocorrelation function of the spatial distribution of the refractive index. In the second case the horizontal dimensions of the regions in question in relation to those of the associated Fresnel zones are of importance. The second part of the article discusses the mathematical treatment of fading phenomena which, in general, involve the superposition of a constant and a fluctuating component. Joint Gaussian distributions for more than one variable are essential here. As an example, the rapidity of the fading of amplitude and phase of one and the same received signal are discussed and compared to each other.

2809*: B. Combée and P. J. M. Botden: Image intensification in medical X-ray technology (Tools of biological research, pp. 154-159; Blackwell, Oxford 1959).

After a brief survey of the evolution of X-ray techniques since 1895, the operation of the X-ray image intensifier is explained. Different versions of the intensifier are discussed and illustrated with photographs. The X-ray image intensifier has opened the way to novel diagnostic techniques hitherto not feasible. Further developments are expected, in-

cluding X-ray supervision during surgical operations.

- 2810:** J. L. Melse and P. Baeyens: Protecting silver and copper against tarnishing by means of a chromate passivating process (46th Annual Technical Proceedings, pp. 293-297, American Electroplaters' Society, Newark N.J. 1959).

The paper describes the experimental work that forms the basis of improvements in methods of obtaining protection of silver or copper by immersion in solutions of hexavalent chromium compounds. To obtain good passivation consistently, without interfering appreciably with the solderability of either silver or copper, certain metal-complexing agents are added to the hexavalent chromium solution so as to maintain a defined relationship between the pH value of the solution and the metal-solution potential.

- 2811:** P. C. van der Linden and J. de Jonge: The preparation of pure silicon (Rec. Trav. chim. Pays-Bas **78**, 962-966, 1959, No. 11).

An apparatus is described for the preparation of pure silicon by thermal decomposition of trichlorosilane on a hot tantalum wire in a hydrogen atmosphere. The polycrystalline silicon is obtained in the form of rods with a diameter of about 15 mm and a length of 20-40 cm. The yield of Si is 45-50% if calculated on the Si-content of SiHCl_3 . From resistivity measurements, the boron content of the silicon obtained can be calculated to be $0.5 \times 10^{-6} \%$ (resistivity of single crystals about 300-500 ohm.cm, p-type).

- 2812:** H. C. Hamaker: Adjusting single sampling plans for finite lot size (Appl. Statistics **8**, 210-214, 1959, No. 3).

Most single sampling plans assume that the lot size is large compared with the sample size, and the calculated operating characteristic curves are strictly valid only under these conditions. This article describes a simple method for finding the sample size and acceptance number appropriate to a lot of finite size, so that the resulting operating characteristic curve closely approximates to that for a given plan with an infinite lot.

- 2813:** J. Davidse: N.T.S.C. colour-television signals (Electronic and Radio Engr. **36**, 370-376 and 416-419, 1959, Nos. 10 and 11).

Investigations into the choice of parameters for an N.T.S.C. colour-television system have shown that the statistical properties of the signal are of importance. This article deals with measurement

techniques and circuits used to obtain the required statistical data. The results are mentioned of a large number of measurements, using signals obtained by scanning colour slides and also camera signals. The author deals successively with the distribution of the colour information over the two colour signals, the distribution of the instantaneous level of the sub-carrier amplitude, and the distribution of the instantaneous level of the luminance signal. The bearing of the results on the transmission of colour-television signals is briefly commented on.

- 2814:** J. A. Greefkes and F. de Jager: Voice radio systems for high noise paths (Electronics **32**, No. 50, 53-57, 1959).

Description of two Frena systems for speech transmission. The original signal is split into its frequency and amplitude components, the two types of information are transmitted on separate channels, and are then recombined into the original sound. This system is highly insensitive to noise, and can thus be used where the level of interference is high. Block diagrams and circuits for transmitter and receiver are given. See also Philips tech. Rev. **19**, 73-83, 1957/58.

- 2815:** H. Koopman, J. H. Uhlenbroek, H. H. Haack, J. Daams and M. J. Koopmans: Investigations on herbicides, II. 2-alkyloxy- and 2-aryloxy-4,6-dichloro-1,3,5-triazines; 2-alkylthio- and 2-arylthio-4,6-dichloro-1,3,5-triazines (Rec. Trav. chim. Pays-Bas **78**, 967-980, 1959, No. 11).

An improved synthesis of 4,6-dichloro-2-phenoxy-1,3,5-triazine from cyanuric chloride and phenol in the presence of collidine (2,4,6-trimethylpyridine) induced the authors to investigate the scope and limitation of the substitution of one chlorine atom in cyanuric chloride and the influence of the base used as an acid acceptor. Phenols, thiophenols, alcohols, thiols and oximes generally reacted with cyanuric chloride in the presence of collidine giving good yields of the corresponding substitution derivatives. The herbicidal and fungicidal properties of the compounds are dealt with and briefly discussed. The influence of the alkyl or aryl side chain on the biological activity was determined. For this reason some derivatives mentioned in the literature were included for comparison in the biological tests.

- 2816:** A. Verloop, A. L. Koevoet, R. van Moorseelaar and E. Havinga: Studies on vitamin D and related compounds, IX. Remarks on the iodine-catalysed isomerizations of vitamin D

and related compounds (Rec. Trav. chim. Pays-Bas **78**, 1004-1014, 1959, No. 11).

As a sequel to previous publications, details are given on the iodine-catalysed reactions of previtamin D, tachysterol, cis- and trans-vitamin D (influence of solvent, concentration, wavelength of light). The possibility of a previtamin D determination based on the cis/trans isomerization is indicated. Some results and products obtained from the iodine-catalysed reactions in the vitamin D₃ series are reported.

2817: M. J. Sparnaay: Gas adsorption on germanium surfaces (Solid state physics in electronics and telecommunications, Proc. int. Conf., Brussels, June 1958, edited by M. Désirant and J. L. Michiels, Vol. I, pp. 613-618, Academic Press, London 1960).

Physical adsorption, mainly of argon gas, was used as a tool for investigations concerning germanium surfaces. It appeared in the measurements that the amount of gas adsorbed at a certain temperature and pressure depends on the oxygenated state of the surface. From the adsorption isotherms at different temperatures thermodynamic quantities can be derived and conclusions can be drawn concerning the behaviour of the adsorbed gas on the different adsorbents.

2818: C. Wansdronk: On the influence of the diffraction of sound waves around the human head on the characteristics of hearing aids (J. Acoust. Soc. Amer. **31**, 1609-1612, 1959, No. 12).

A small hearing aid, hanging in an anechoic room, is made to drive an AVC circuit, the output signal of which is conducted to a power amplifier and loudspeaker and can be recorded on a tape. During playback of this tape, with the output of the recorder connected to the power amplifier, the same sound field as existed around the hearing aid is reproduced. If the hearing aid is placed on a person in the position where it is to be worn and that person is situated so that the hearing aid is at the same point as during the recording, the output of the hearing aid during playback of the tape will indicate the influence of the diffraction around the human head.

Three specimens of hearing aid were measured on different people. The results showed that there exists a large difference between the hearing aids but no fundamental differences between the persons.

The curves plotted for males and females showed the same trend, and no correlation was found with the hairdress. No success was achieved in an attempt to replace the human head by a simple model, such as a wooden sphere or a wooden box, the agreement of the diffraction phenomena between model and head being too poor.

2819: H. Koelmans and H. G. Grimmeiss: The photoconductivity of CdIn₂S₄ activated with Cu or Au (Physica **25**, 1287-1288, 1959, No. 12).

Polycrystalline CdIn₂S₄ was prepared by heating equimolecular quantities of pure CdS and In₂S₃ in sulphur vapour at 1150 °C. The absorption limit was found to be at 2.2 eV. The dark resistance of the samples proved to be dependent on the sulphur pressure. Unactivated samples showed photoconductivity with a spectral response peak at 2.1 eV. Activation with Cu or Au (optimum molar concentration approx. 2×10^{-3}) increased the photoconductivity by a factor of 10³. The decay time of the photocurrent was about 10⁻³ sec. The dependence of the photocurrent on the light intensity was found to be linear in the lower and higher intensity ranges, and superlinear in a transition range. By grinding-off part of the samples, crystals were obtained that showed the same sensitivity over the whole range as the untreated samples under strong illumination.

2820: A. E. Korvezee and J. L. Meijering: Validity and consequences of Schreinemakers' theorem on ternary distillation lines (J. chem. Phys. **31**, 308-313, 1959, No. 2).

In about 1900 Schreinemakers showed that the distillation lines of a ternary mixture, i.e. the loci of the points in the ternary diagram indicating the composition of the liquid phase during distillation, are tangential at their end points to one of the sides of the triangle. This was recently disputed by Redlich and Kister. In this paper a further proof is given of the correctness of Schreinemakers' theorem. Certain parameters are defined that govern the form of the distillation lines in each corner of the composition triangle. The values of these parameters can in principle be derived from accurate binary boiling-point curves. The occurrence of distillation lines with one or two points of inflection in a ternary system without complications from azeotropes or demixing is discussed at some length.